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THE COEFFICIENT OF VISCOSITY OF SULPHUR DIOXIDE OVER A LOW TEMPERATURE RANGE[1]

By W. W. Stewart[2] and O. Maass[3]

Abstract

The coefficient of viscosity of sulphur dioxide has been measured over a temperature range from 30° to −75°C. The method and apparatus used are similar to those described by Sutherland and Maass (5). All values for the viscosity are referred to air at 23°C. The measured values for the viscosity between 0°C. and 30°C. agree within the experimental error, about 0.1%, with the values published by Trautz and his coworkers. At temperatures below 0°C. the values obtained for the viscosity are important, as they supply data on the viscosity of sulphur dioxide which heretofore have not been available in the literature.

Introduction

This paper discusses the results of the preliminary work on the measurement of the coefficient of viscosity of sulphur dioxide. From a survey of the literature it is quite evident that values for the viscosity of this gas are not available at temperatures below 0°C. These data are essential in order that the validity of equations of state, which depend on viscosity measurements, *e.g.*, the equation of state of Maass and Mennie (2), may be tested over an extended temperature range.

This research is being continued and, when the present apparatus has been reconditioned, may result in slight changes being made in the present values for the viscosity at the lower temperatures, but at present these results are accurate enough to test the validity of the equations of state with the present P.V.T. data available for sulphur dioxide.

In conjunction with this research the density of sulphur dioxide is being determined with a high degree of accuracy at low pressures, in order to obtain the P.V.T. data necessary to study the relationship between the coefficient of viscosity and the gas laws.

The viscosity of sulphur dioxide has been measured by an oscillation disk method. The apparatus and method are similar to those described by

Sutherland and Maass (5) in a recent publication. The reader is referred to that paper for the complete details of this method.

The only change that has been made in the original apparatus has been in connection with the auxiliary lighting arrangement. The system has been improved by focusing the image of a slit, cut in a brass plate, on the scale. The slit is illuminated by a 200-watt tungsten lamp mounted behind the brass plate in a horizontal position, so that the filament of the lamp is vertical. The light from the slit is concentrated on the mirror by a lens, the image of the illuminated slit being reflected from the mirror and focused on the scale. This image on the scale was about 1 cm. wide with sharply defined edges; it illuminated the markings on the scale sufficiently so that the position of the edge could be observed with an accuracy better than ± 0.2 mm. when the disk was oscillating.

The sulphur dioxide was purified by condensing it from a tank of c.p. material in a bulb immersed in a carbon dioxide snow-ether bath, and distilling under vacuum in an air-free apparatus until the vapor pressures of two successive fractions were the same. This was indicated on a differential manometer placed between two condensation bulbs, so arranged that they could both be immersed in the same constant-temperature bath. The bath was well stirred and held at −10°C., at which temperature the absolute vapor pressure of sulphur dioxide is about one atmosphere. After three or four distillations the vapor pressures of two successive fractions did not differ by an amount that could be read on the differential manometer. All the gas was tested in this manner before it was distilled into the storage bulbs.

The apparatus was filled with the pure sulphur dioxide at room temperature after flushing out the apparatus several times with the pure gas. Before any observations were made time was allowed for the gas to come to the temperature of the bath. At temperatures below the normal boiling point of the gas, about −10°C., the pressure was reduced. The coefficient of viscosity of a gas is independent of the pressure, so the results obtained at low pressures are comparable with those measured at atmospheric pressure.

Results

The value for the viscosity of the gas is calculated from the expression

$$\eta = \frac{\lambda - x}{C t},$$

where η is the coefficient of viscosity; λ is the "log. dec." calculated from the observed amplitudes of the oscillating disk; x is the "log. dec." due to the friction of the wire and is a constant; C is a constant depending on the dimensions of the apparatus; and t is the time in seconds for one complete oscillation of the disk.

The value for the constant x has been taken as 0.000173 as determined experimentally by Sutherland and Maass (5).

The constant C is obtained by calibrating the apparatus with a gas, such as air, having a known viscosity. The viscosity of air at room temperature has been determined by many investigators, but the value of the viscosity of air

used in this case was Millikan's (3) most probable value for air at 23°C., namely, 1824.0×10^{-7} C.G.S. units, with an error not greater than 0.1%. To obtain the value of the viscosity of air at any temperature between 17° and 30°C. the expression given by Millikan has been used,

$$\eta_t = 1824.0 \times 10^{-7} - 4.93 \times 10^{-7} (23° - t).$$

The air was purified by passing it through solutions of potassium hydroxide, sulphuric acid and over phosphorus pentoxide.

The average value of C obtained from five completely independent observations was 4.6142. The deviation from the mean value of each determination was less than ± 0.0013 or less than 0.03%.

The results of the measurements of the coefficient of viscosity of sulphur dioxide, using the values of the two constants which have been given above, are shown in Table I. The value λ is obtained from a set of observations each involving at least ten complete oscillations, and in some cases two or more sets of readings have been averaged.

TABLE I

RESULTS OF MEASUREMENTS OF THE COEFFICIENT OF VISCOSITY OF SULPHUR DIOXIDE

Temp., °C.	t, sec.	Press., mm.	λ	$\lambda - x$	$\eta \times 10^{-7}$
29.8	51.100	760	0.031335	0.030604	1298.0
29.5	51.100	760	0.031285	0.030554	1295.8
29.3	51.100	760	0.031282	0.030551	1295.6
20.5	51.095	760	0.030320	0.029589	1255.0
20.4	51.110	760	0.030285	0.029554	1253.2
20.2	51.100	760	0.030252	0.029521	1252.0
0.0	51.055	760	0.028013	0.027282	1158.0
− 5.1	51.065	733	0.027435	0.026704	1133.3
− 6.2	51.070	733	0.027408	0.026677	1132.0
− 7.5	51.055	733	0.027257	0.026526	1126.0
−17.9	51.045	474	0.026261	0.025530	1083.9
−19.2	51.040	450	0.026176	0.025445	1080.6
−20.3	51.030	430	0.026086	0.025355	1076.8
−35.6	51.010	105	0.024592	0.023841	1013.6
−36.5	51.010	105	0.024531	0.023800	1011.2
−75.0	51.000	8	0.020926	0.020195	858.1

TABLE II

COMPARISON OF THE EXPERIMENTAL VALUES OBTAINED IN THIS WORK FOR THE VISCOSITY OF SULPHUR DIOXIDE WITH THOSE OF OTHER INVESTIGATORS

Temp., °C.	$\eta \times 10^{-7}$		
	Observed in present work	Published previously	
0.0	1158.0	1225	Graham, 1846 (1).
		1183	Vogel, 1914 (8).
		1168	Smith, 1922 (4).
14.0	1221.5	1221	Trautz and Weizel, 1925 (6).
17.4	1238.2	1242	Trautz and Zink, 1930 (7).
17.7	1239.0	1239	Trautz and Weizel, 1925 (6).
18.0	1241.0	1253	Smith, 1922 (4).
20.0	1251.0	1380	Graham, 1846 (1).

The average error in the value of the viscosity due to the experimental error is taken to be about 0.1% at any one temperature.

The temperature-viscosity relationship of sulphur dioxide is shown in Fig. 1.   The curve shows the viscosity as a function of the temperature and has been plotted by using the values for the viscosity given in Table I.   From this curve values for the viscosity have been determined at temperatures at which no experimental value was observed, so that a comparison could be made with the published data on the viscosity of sulphur dioxide.

Table II shows the experimental values for the viscosity of sulphur dioxide in comparison with the published data.
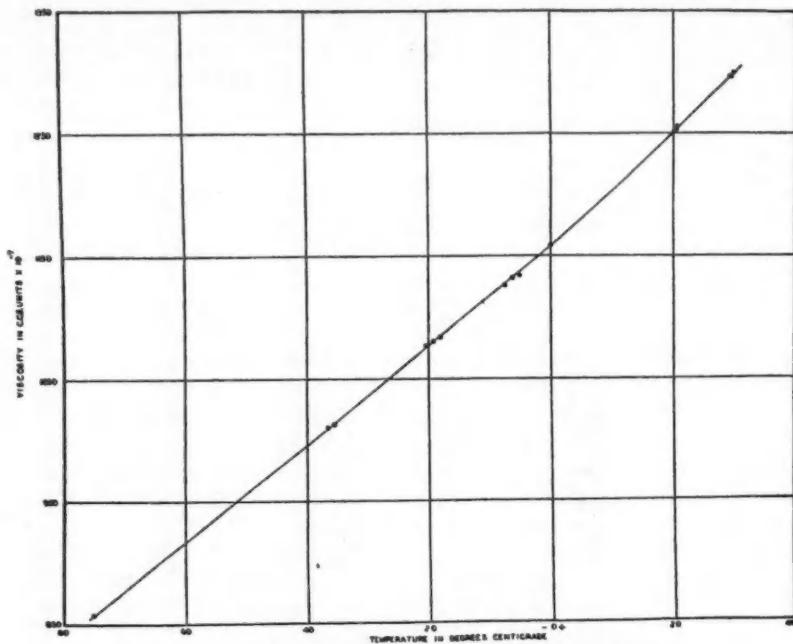
FIG. 1.   *Temperature-viscosity relationship of sulphur dioxide.*

At room temperature the observed values for the viscosity of sulphur dioxide are in excellent agreement with the most recent results, those of Trautz and his coworkers.   Smith's values at 0°C. and 18°C. are about 1% too large, but the error in Smith's values was as large as 3%.   Vogel's value at 0°C. is also too large by about 2.5%.   The values published by Graham, which are the values given in most of the tables of physical constants, are undoubtedly too large. At the lower temperatures there are no published data for comparison.   The observed values are therefore valuable, as they supply data on the viscosity of sulphur dioxide, which, until the completion of this work, had not been available in the literature.

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THE CRITICAL TEMPERATURES AND PRESSURES OF THE THREE TWO-COMPONENT SYSTEMS COMPRISED OF CARBON DIOXIDE, METHYL ETHER AND PROPYLENE[1]

By C. A. WINKLER[2] and O. MAASS[3]

Abstract

The so-called critical temperatures and critical pressures for two-component systems are defined. For the first time three two-component systems have been investigated, involving three components taken two at a time. The three components were propylene, methyl ether and carbon dioxide. An experimental technique involving several new features is described. Accuracy in the determination of both critical temperatures and pressures is claimed. The system sulphur dioxide-methyl ether was also examined and the conclusions of previous investigators regarding compound formation confirmed. The results of the other three systems are analyzed and a theoretical discussion of these results reserved for a later publication.

The Investigation of Critical Phenomena in Gaseous Binary Mixtures

Many and varied have been the investigations on the relationships existing between pressure, temperature and volume, in two-component systems. Among the best publications on the subject are those of Kuenen (7, 8, 9, 10) and Caubet (2, 3, 4). Both of these writers deal with the theoretical aspects of the subject in a well-organized, comprehensive manner. They have no record, however, of having studied the systems carbon dioxide-methyl ether, carbon dioxide-propylene, or methyl ether-propylene. A thorough search of the literature revealed no reference to the last two systems, while the carbon dioxide-methyl ether system has been investigated only to a slight extent.

Briner and Cardoso (1) determined, in part, the pressures for initial and completed liquefaction for three mixtures of carbon dioxide and methyl ether at three different temperatures, and they remarked that the gases do not form a molecular compound. No reference is made, however, to the retrograde condensation which is to be noticed in a binary gaseous mixture at the critical region.

In the investigation of the velocity of reaction by Sutherland and Maass a definite discontinuity was established at the critical temperature. P. V. T. data for two-component systems at the critical temperature are not available in the literature. This investigation is the first step towards P. V. T. determinations in the critical temperature region.

Experimental

Description of Apparatus

The apparatus employed for this investigation was essentially that described by Sutherland and Maass (14); and is diagrammatically represented in

Fig. 1. By careful reconstruction the mechanical difficulties were considerably reduced.
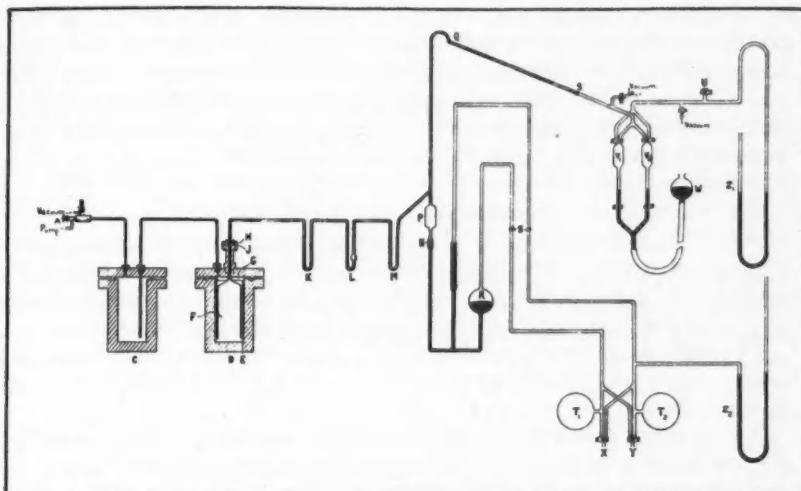
FIG. 1. *Diagram of apparatus.*

The bombs C and D, machined from shafting steel, and each of a capacity of approximately half a litre, were provided with covers having two apertures as indicated in the diagram.   Six half-inch steel bolts served to fasten the cover securely to the bomb.   The grooved lead gaskets, shown in the figure, when coated with a thin layer of commercial graphite composition, served to prevent leaks between the bomb and cover, over the entire range of pressures used.

Into the bomb, D, a Pyrex glass bell, F, was inserted, to which was sealed the heavy-walled Pyrex capillary tubing KLM (outside diameter, 7.5 mm.). The capillary tubing passed through a steel pipe screwed into the cover of the bomb, this pipe being 3 in. long, with a bore of 8 mm., and having a $2\frac{1}{2}$-in. flange at its upper end, as shown.   A steel cover into which was fitted a steel plate, H, and a rubber disk, J, was bolted to the flange.   By tightening four bolts passing through the cover, the rubber disk was compressed between the steel plate and the lower flange.   In this way, the rubber was extruded slightly around the capillary tubing, and forced tightly against it, effecting a seal between the glass and metal portions of the apparatus.   Great care had to be taken to prevent unequal pressure on any one portion of the steel plate, otherwise the glass was easily sheared.   The seal obtained was quite impervious to mercury, even at pressures up to 125 atm.

To prevent shearing of the glass bell from the capillary tubing as a result of side-sway, at the point where the latter enters the bomb, a steel pipe, E, of internal diameter slightly larger than the external diameter of the bell, was screwed into the cover.   At intervals around the bottom of this pipe, small

screws were inserted. These could be adjusted to bear lightly against the bell, so that all horizontal motion of the latter was prevented.

Shearing of the bell from the capillary at the same point was also possible by a slight vertical motion. This was especially noticeable at the higher pressures. To overcome this difficulty a thick rubber disk, G, was inserted between the bell and the cover of the bomb, surrounding the capillary tubing. The tubing was also slightly expanded at the point where it passed through the rubber disk in the glass-metal seal. The careful observance of these precautions eliminated a great deal of the mechanical difficulty hitherto encountered in this apparatus.

The bomb, C, was approximately two-thirds filled with carefully purified mercury, the remainder of the volume being filled with oil from the Cailletet compression pump. The bomb, D, was filled with mercury only. This combination of the bombs prevented oil from reaching the bomb, D, ensuring contact of the gaseous mixture with mercury and glass surfaces only.

The bulb, L, in which the observations were made, was of the shape illustrated merely for convenience of operation, as will be evident from the method of manipulation.

The diagram is practically self-explanatory in so far as the remainder of the apparatus is concerned. The Pyrex and soft glass portions of the apparatus were connected by DeKhotinsky joints, S. The volumes T_1 and T_2 served to facilitate pressure control.*

Manipulation of the Apparatus

Preparatory to making a determination, mercury was pumped from the bomb D through the capillary tubing, until it slowly dropped into the volume P. The mercury in M was then frozen in a solid carbon dioxide-acetone mixture, and the remainder of the apparatus evacuated. The gases were admitted individually through the stopcock, U, one gas being permitted to enter the volume V_1 and the other to enter the volume V_2, V_1 and V_2 being of the same capacity. The relative amounts of the gases taken were determined on the open manometer Z_1.

The two-way stopcocks on V_1 and V_2 were then reversed, and the reservoir, W, raised until the mercury reached the point Q. This forced the gases over into the volume, P, after which the stopcocks on V_1 and V_2 were closed. In this manner the gases were contained between the two mercury columns in the capillary tubing, and the mercury in P. Thus, contamination of the mercury in the bombs by traces of stopcock lubricant was avoided.

The mercury in the seal, M, was then permitted to liquefy, and the pressure on the valve, B, reduced simultaneously with the application of a slight pressure to the reservoir R through the stopcock at X. The mercury, rising in P, forced the gas into the glass bell in the bomb D. The mercury from P was permitted to pass along the capillary tubing until it dropped through the smaller into the larger expansion of the bulb at L, whereupon the mercury at

* *The apparatus, as diagrammatically represented, is also intended for future investigations of somewhat different nature, and includes some features which could be dispensed with for the present purpose.*

M was again rapidly frozen. The small amount of mercury remaining in the larger bulb could be drawn into the bomb by first compressing slightly the gases in the bulb, followed by a sudden expansion. The gaseous mixture could then be compressed to the desired extent by means of the Cailletet pump. The pressures were determined on a calibrated Bourdon gauge.

The temperature of the compressed gaseous mixture was controlled by an electrically heated, well-agitated bath of glycoline oil. A lamp-bank resistance in parallel with the heating element gave any desired rate of temperature increment.

Preparation and Purification of the Gases

The carbon dioxide was obtained by sublimation of the solid. The sublimate was passed over phosphorus pentoxide and condensed in a bulb immersed in a solid carbon dioxide-acetone freezing mixture maintained under reduced pressure. This method was adopted to produce slow condensation of the gas, thus avoiding, to a large extent, the occlusion of an appreciable quantity of air in the condensate. The solid so obtained was resublimed and the gas further dried over phosphorus pentoxide, after which it was admitted to the storage flask, which previously had been carefully flushed with carbon dioxide and evacuated.

The critical temperature of the gas was determined as a check on the purity. A value of 31.2°C. was obtained, indicating a sufficiently high degree of purity for the present investigation.

The methyl ether was prepared by the treatment of methyl alcohol with concentrated sulphuric acid. The acid was heated to 135°C. and the alcohol introduced under the surface, a procedure which was found to minimize the loss of methyl ether. The temperature was maintained at approximately 135°C., and the distillate, after passing through a water-jacketed condenser which removed a considerable quantity of alcohol, was passed through concentrated sulphuric acid saturated with methyl ether, and finally through anhydrous calcium chloride, which served to remove traces of alcohol. The methyl ether was finally condensed, using a solid carbon dioxide-acetone mixture. It was then fractionated at a low temperature, the middle fraction being passed over phosphorus pentoxide and condensed in a bulb fitted with a stirrer actuated by a solenoid. The ether was subjected to three further fractionations before being admitted to the carefully flushed 'and evacuated storage flask.

The critical temperature of the methyl ether thus prepared was found to be 126.2°C., a value in substantial agreement with that of Tapp (15), who, with an apparatus differing from that of the authors, obtained a value of 126.1°C. for various samples prepared by the above method. The critical pressure was found to be 53.0 atm.

Propylene was prepared by the dehydration of isopropyl alcohol over alumina at 360°C. and purified by low temperature fractionation, as described by Coffin and Maass (5, 6) and Maass and Wright (11, 12). The purity of the propylene was checked by vapor pressure measurements during fractionation,

and by determination of the critical temperature, for which a value of 92.9°C. was obtained. Since this is in agreement with that found by Maass and Wright (11) who report a value of 92.1°C., the gas was used without further purification.

Determination of the Vapor Pressures of the Binary Mixtures

When the gaseous mixture had been brought into the glass bell contained in the bomb D, and the mercury seal, M, frozen, pressure was applied until partial liquefaction occurred. The temperature of the oil bath surrounding the bulb at L was then slowly increased, care being exercised to prevent appreciable lag of the temperature inside the bulb relative to that of the bath. As the temperature was raised, the pressure being maintained at a constant value, the amount of liquid slowly decreased. The temperature at which the liquid phase just disappeared was regarded as that corresponding to the pressure of the vapor as registered on the Bourdon gauge. The observations were considerably facilitated with the aid of a telescope, which enabled minute traces of liquid to be seen.
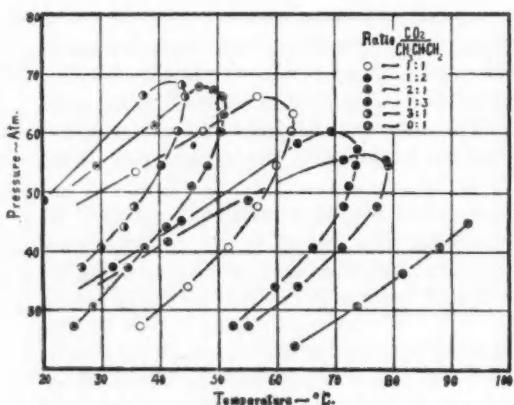
The Bourdon gauge was calibrated, over a range up to 70 atm., against the vapor pressure of pure carbon dioxide, and the necessary corrections, obtained from a calibration curve, applied to all subsequent pressure readings.

After each successive observation, the pressure was increased slightly until liquid again appeared, and the corresponding temperature for disappearance of the meniscus determined as before.

FIG. 2. *Pressure-temperature relationships for the system carbon dioxide-methyl ether.*

FIG. 3. *Pressure-temperature relationships for the system carbon dioxide-propylene.*

The pressures corresponding to complete liquefaction or condensation at various temperatures were also determined for each mixture investigated. This was done by maintaining the temperature at a given value, and slowly increasing the pressure until only a trace of gaseous mixture remained. It was absolutely essential that the system be permitted to attain equilibrium. To ensure this, the cross hair in the eyepiece of the telescope was focused on the boundary surface of the gas bubble. If, after some time, no increase or decrease in the size of the bubble had occurred, it was assumed that equilibrium had been attained.

In all cases, the temperatures were ascertained on standardized thermometers with an error not exceeding 0.1°C.

The results obtained for a mixture of a given ratio of components were checked, using a second mixture of the same composition. Duplicate determinations were required to agree within 1.0°C. and 2 atm. in the case of the carbon dioxide and methyl ether curves, these being the first to be determined. For the mixtures of carbon dioxide and propylene, and those of propylene and methyl ether, it was found that agreement within 0.5 and 1 atm. could be obtained, by measuring out larger amounts of the gases, although maintaining the desired ratio.

Results and Discussion

The results obtained for the determinations of the vapor pressures, and the pressures required for complete condensation, at various temperatures, are given in Tables I-VI, and graphically represented in Figs. 2-4, inclusive.
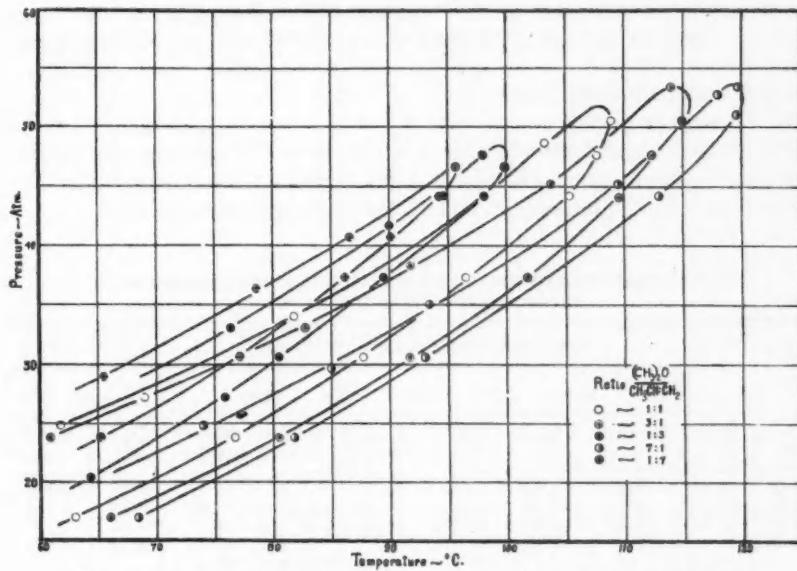
FIG. 4. *Pressure-temperature relationships for the system methyl ether-propylene.*

TABLE I

THE VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE SYSTEM
CARBON DIOXIDE-METHYL ETHER

Pressure, atm.	Temperature (°C.) for disappearance of meniscus for ratio of carbon dioxide to methyl ether of:				
	1:1	1:2	2:1*	1:3	3:1
17.0	45.1	....	....	....	....
20.4	....	57.5	....	64.5	34.9
23.8	....	62.3	....	....	....
27.2	55.0	66.0	45.2	73.8	....
30.6	58.5	70.8	....	....	....
34.0	....	76.3	52.3	82.8	44.0
37.3	65.6	79.9	....	85.7	45.4
40.7	....	....	59.0	89.1	49.1
44.2	72.3	86.2	....	92.5	....
47.6	....	....	65.0	95.0	53.3
51.0	78.2	90.4	....	97.5	....
54.4	80.3	91.6	67.8	....	57.6
57.2	82.0	92.6	....	100.4	....
60.2	82.7	....	71.0	103.0	60.3
63.1	....	93.8	71.8	....	61.2
66.2	85.0	94.3	72.1	104.7	62.2
69.6	....	....	73.0	104.5	62.9
73.0	86.0	94.0	....	100.0	63.4
76.4	84.1	89.0	72.4?	....	54.0?
78.0	70.0	....	....	....	....

* This curve was not checked.

The upper portion of each curve represents the trend of the pressure values for complete condensation at the temperatures indicated, while the lower portion represents the increase in vapor pressure of the mixture with increasing temperature. It is to be noticed that the condensation curve and vapor pressure curve are really continuous.

If, for a given pair of components, a line is drawn tangentially to all the curves at their upper extremities, the point of contact of this line (the critical line) with a given curve is known as a plait-point on that curve. The corresponding temperature may be termed the plait-point temperature.

TABLE II

THE CONDENSATION PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE
SYSTEM CARBON DIOXIDE-METHYL ETHER

Ratio of carbon dioxide to methyl ether									
1:1		1:2		2:1		1:3		3:1	
Temp. °C.	Press. atm.	Temp. °C.	Press. atm.	Temp. °C.	Press. atm.	Temp. °C.	Press. atm.	Temp. °C.	Press. atm.
34.0	54.4	41.0	54.4	30.0	62.2	31.0	46.2	32.0	69.6
39.0	57.2	51.0	59.0	42.2	71.8	44.0	51.0	42.0	76.4
50.0	64.8	64.0	65.5	58.0	81.0	59.0	57.2	51.6	79.7
60.0	73.0	77.0	73.8	....	....	72.8	63.1	59.6	79.0
...	...	....	....	....	....	80.5	67.2	....	....

The temperature corresponding to a tangent drawn parallel to the pressure axis at the point of maximum abscissa of a given curve has been termed the critical contact temperature. Above this temperature liquefaction was found to be impossible, regardless of the magnitude of the pressure applied. As Kuenen (7, 8, 9, 10) and Caubet (2, 3, 4) have pointed out, however, this point does not represent a true critical temperature, since such a mixture possesses a critical region. The considerations leading up to this conclusion may be briefly outlined, as applied to the observations made in the present work.

At temperatures below the plait-point temperature, condensation was regular, inasmuch as the quantity of liquid phase increased regularly during compression, until the mixture was completely liquefied. Between the plait-point and critical contact temperatures, the condensation was characterized initially by an increase in the amount of liquid present as the pressure was

TABLE III

THE VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE SYSTEM CARBON DIOXIDE-PROPYLENE

Pressure, atm.	Temperature (°C.) for disappearance of meniscus for ratio of carbon dioxide to propylene of:				
	1:1	1:2	2:1	1:3	3:1
27.2	36.5	52.5	25.1	55.1	18.3
34.0	44.8	59.7	....	63.6	....
37.3	....	....	34.6	....	26.6
40.7	51.8	66.3	37.4	71.2	30.0
44.2	....	....	41.2	....	34.0
47.6	56.8	71.5	....	77.2	35.7
51.0	....	72.3	45.6	....	....
54.4	60.0	73.6	48.3	79.1	40.3
55.4	....	....	....	78.8	....
57.2	....	73.9	....	....	....
60.2	62.6	....	50.5	....	43.3
63.1	63.0	....	51.1	....	....
66.2	56.8	....	50.9	....	44.4
67.2	....	....	49.3	....	....
68.2	....	....	....	....	44.0

TABLE IV

THE CONDENSATION PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE SYSTEM CARBON DIOXIDE-PROPYLENE

Ratio of carbon dioxide to propylene									
1:1		1:2		2:1		1:3		3:1	
Temp., °C.	Press., atm.	Temp., °C.	Press., atm.	Temp., °C.	Press., atm.	Temp., °C.	Press., atm.	Temp., °C.	Press., atm.
36.0	53.4	32.0	37.3	29.4	54.4	41.4	40.7	20.2	48.6
47.5	60.2	43.8	45.2	39.2	61.2	55.2	48.6	37.2	66.4
....	....	63.6	58.2	46.9	67.9	71.5	55.4	....	....
....	....	69.4	60.2	....	....	....	....	....	....

TABLE V

THE VAPOR PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE SYSTEM METHYL
ETHER-PROPYLENE

Pressure, atm.	Temperature (°C.) for the disappearance of the meniscus for the ratio of methyl ether to propylene of:				
	1:1	1:3	3:1	1:7	7:1
17.0	63.0	....	66.0	....	68.4
20.4	....	64.3			
23.8	76.7	....	80.5	65.2	81.8
27.2	....	75.9	....	....	....
30.6	87.7	80.5	91.7	77.2	93.1
37.3	96.5	89.5	101.8	86.2	....
40.7	....	....	....	90.1	....
44.2	105.4	98.1	109.6	94.2	113.0
46.6	....	99.9	....	95.6	....
47.6	107.7	....	112.4	....	....
51.0	108.9	....	115.0	....	119.6
53.4	....	....	114.0	....	119.4

TABLE VI

THE CONDENSATION PRESSURE-TEMPERATURE RELATIONSHIPS FOR THE SYSTEM
METHYL ETHER-PROPYLENE

Ratio of methyl ether to propylene									
1:1		1:3		3:1		1:7		7:1	
Temp.	Press.	Temp.	Press.	Temp	Press.	Temp.	Press.	Temp.	Press.
61.8	24.8	76.4	33.0	60.8	23.8	65.5	28.9	74.0	24.8
69.0	27.2	90.0	41.7	82.8	33.0	78.6	36.3	85.0	29.6
81.8	34.0	94.7	44.2	91.8	38.3	86.6	40.7	93.4	35.0
103.3	48.6	98.0	47.6	103.6	44.2	....	....	109.5	45.2
....	....	....	....	....	....	....	....	118.0	52.7

increased, until the pressure corresponding to the critical point of contact was
attained. For pressures greater than this value the liquid phase decreased in
amount, and ultimately disappeared. This phenomenon has been called, by
Kuenen, retrograde condensation.

It is evident from these considerations that a single critical point cannot
be ascribed to a mixture, but that the plait-point and critical contact temper-
atures may be regarded as limiting a critical region.

The differences existing between the critical temperature as calculated, and
the plait-point and critical contact temperatures for the three systems in-
vestigated are shown in Fig. 5. The last two named temperatures were
ascertained from the corresponding curves in Figs. 2–4. The calculated
critical temperatures were determined from the law óf mixtures, formulated
by Pawlewski (13) as follows:

$$T_c = \frac{n t_c' + (100-n)\, t_c''}{100} ,$$

where T_c is the critical temperature of the mixture containing $n\%$ by weight
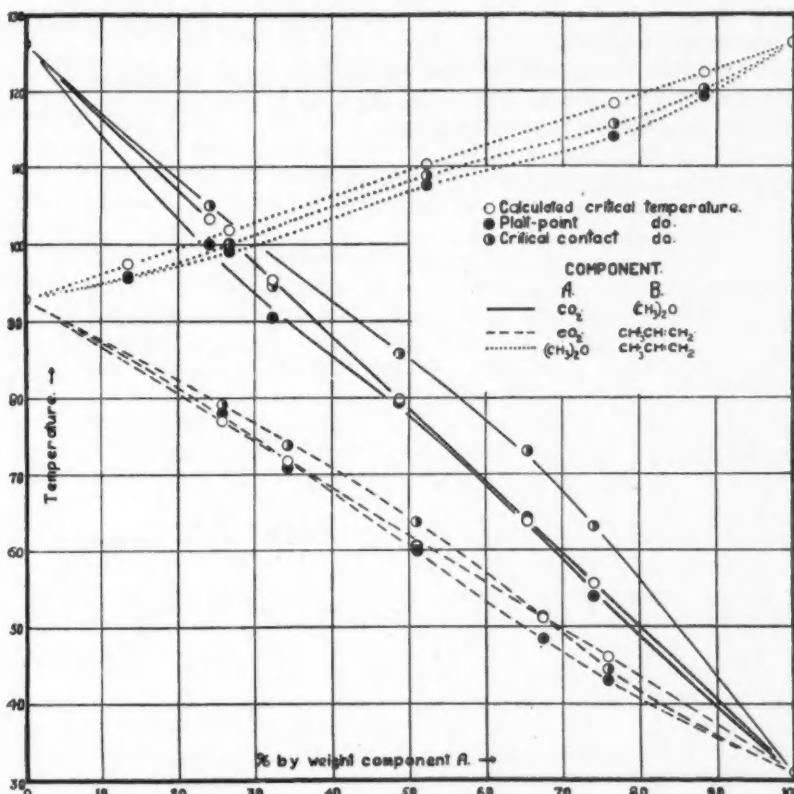
FIG. 5.   Comparison of the calculated critical temperature, and the plait-point and critical-contact temperatures, for the systems carbon dioxide-methyl ether, carbon dioxide-propylene and propylene-methyl ether.

of one component whose critical temperature is t_c', and $(100-n)\%$ by weight of a second component whose critical temperature is t_c''.

The results confirm the contention of Kuenen that considerable deviations from the mixing rule may be encountered. This is rather to be expected, since the law of mixtures does not take into consideration the phenomenon of retrograde condensation.

In Fig. 6 are plotted the plait-point and critical-contact pressures. Here again are to be noted large discrepancies from a straight line relationship.

The fact that retrograde condensation was a prevalent factor in the systems carbon dioxide-methyl ether, carbon dioxide-propylene and methyl ether-propylene, may be taken to indicate the absence of molecular compound formation in any one of these mixtures. Verification of this conclusion was obtained by using a mixture of sulphur dioxide and methyl ether, which

gases Briner and Cardoso (1) have shown to form a molecular compound of the type $(CH_3)_2O.SO_2$.

The sulphur dioxide was obtained by carefully drying the commercial gas, free from sulphur trioxide, and subjecting it to a series of low temperature fractionations as in the case of propylene.
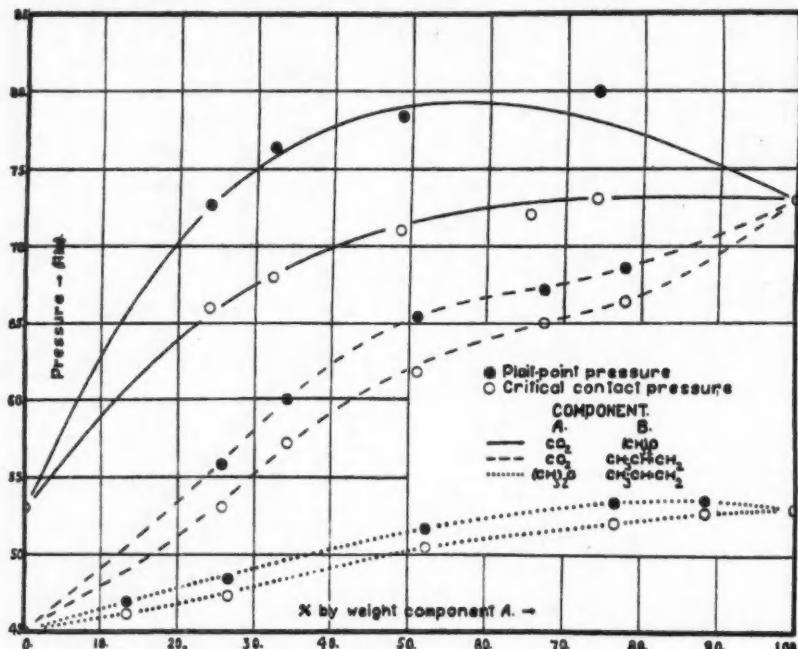
FIG. 6. *The plait-point and critical-contact pressures of the systems carbon dioxide-methyl ether, carbon dioxide-propylene and propylene-methyl ether.*

It was found that for a 1:1 mixture of the gases, the curve of Briner and Cardoso (1) was checked to within 0.5°C. and 1 atm. through the entire range. It proved to be impossible to detect retrograde condensation for this mixture, and the pressure for complete liquefaction was practically the same as that for the initial appearance of a liquid phase. This behavior is characteristic of a pure component.

It is interesting to note that as the difference between the critical temperatures of the components of a mixture diminishes there is a corresponding decrease in the difference between the vapor pressures and the pressures for complete condensation, as may be seen by a comparison of Figs. 2, 3, and 4. Coincident with this decrease, there is to be noticed a smaller critical region.

Fig. 5 also reveals many points of interest. For the system carbon dioxide-methyl ether, the plait-point temperature curve lies consistently below the curve for the calculated critical temperature, but tends to approach the latter

in the region of a 1:1 composition.   The maximum deviation is approximately 4°C.   On the other hand, the critical contact temperature curve lies consistently above that for the calculated critical temperature, and shows a maximum deviation of approximately 8°C. from the latter in the region of 1:1 composition.

In the case of the methyl ether-propylene system both the plait-point and critical-contact temperature curves lie below the curve of the calculated critical temperature, the former curves paralleling one another closely.   Both show tendencies to deviate to the largest extent on either side of a 1:1 composition.

The system carbon dioxide-propylene is striking in so far as both the plait-point and critical-contact temperature curves intersect the calculated critical temperature line, but at opposite sides of a 1:1 composition.   It is noticed that the plait-point temperatures are above the calculated values for amounts of propylene in excess of approximately one-third of the total amount of gas. When the mixture becomes richer in carbon dioxide than corresponds to a ratio 1:2, the plait-point curve falls below the calculated line, and remains below until the pure carbon dioxide point is attained.   The maximum deviation from the calculated values occurs in the region of approximately 75% carbon dioxide.

The critical-contact temperature curve parallels that for the plait-point temperatures, but passes above the calculated line for all mixtures containing less than approximately 67% carbon dioxide.   Above this composition the critical-contact temperature falls below the calculated critical temperature, and remains thus until the pure carbon dioxide point is reached.   The maximum deviation above the calculated line occurs at a composition of about 45% carbon dioxide, while the maximum deviation below the calculated values occurs at about 82% carbon dioxide.

Fig. 6 also shows several features of considerable interest.

In the case of carbon dioxide-methyl ether there is a definite maximum in the plait-point pressures, this maximum being 76.6 atm., i.e., above the critical pressure of either of the components.   This maximum occurs at a composition of approximately 55% carbon dioxide.   The critical-contact pressures do not attain a maximum at compositions intermediate between the pure components, but increase steadily to the critical pressure of pure carbon dioxide.   The maximum discrepancy between the two curves is approximately 16 atm. at a composition of about 50% carbon dioxide.   Neither curve shows points of inflexion, but throughout their course both are above the straight line joining the critical pressure of the pure components.

The system carbon dioxide-propylene exhibits inflexions in the curves of both the plait-point and critical-contact pressures.   Although there is a continual increase in both pressures as the percentage of carbon dioxide is increased, there is a tendency for the values to fall off after a concentration of 50% carbon dioxide until 67% is reached, after which they increase again to the critical pressure of carbon dioxide.   The maximum discrepancy is approximately 7 atm.

For the system methyl ether-propylene there seem to be indications of inflexions, though these are not very definite. The increase is quite steady until a composition of approximately 75% methyl ether is attained, when a slight decrease in the plait-point pressure is in evidence, although the critical contact pressure appears to increase more steadily. A slight inflexion also occurs in the region of about 30% of methyl ether.

In a future communication the authors hope to correlate the observed differences with the intrinsic properties of the components of each of the systems.

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REACTIONS OF ETHYL ALCOHOL ON NICKEL-CHROMIUM CATALYSTS[1]

BY E. H. BOOMER[2] AND H. E. MORRIS[3]

Abstract

A series of catalysts containing nickel and chromium has been prepared and their action on mixtures of ethyl alcohol and water studied. The most active catalysts are prepared by precipitation of the metals as hydroxides or in combination as nickel chromate. The activity of the catalysts depends very much on the nature of the treatment accorded them in preparation. The action of the nickel always predominates but it is more sensitive than chromium to vigorous treatment. The catalysts generally lose some of their activity with use, the nickel more so than the chromium, and the dehydrating efficiency of the catalyst may rise. Secondary reactions, with the production of carbon and complex organic liquids, usually occur, both of which result in carbon dioxide production.

Introduction

The catalytic properties of a given substance or mixture of substances may be examined readily by the use of a suitable reaction. Of a number of reactions available for such studies, one in particular is of wide application, namely, the decomposition of ethyl alcohol. It is well known (13, 17) that most metals and oxides may be classified as to their catalytic properties by this reaction. There are two main types of reaction involving dehydrogenation and dehydration as shown in Equations (1) and (2).

$$C_2H_5OH = CH_3CHO + H_2 \tag{1}$$
$$C_2H_5OH = C_2H_4 + H_2O \tag{2}$$

In general the classification includes those substances promoting dehydrogenation alone, dehydration alone, and those substances with the properties of a mixed catalyst in that both reactions are promoted.

Although the literature regarding the decomposition of ethyl alcohol over simple catalysts is extensive, comparatively little has been done with mixtures of catalysts. Such mixtures are of interest because of their relation to promoted and supported catalysts which have been widely investigated (12). Furthermore the study of reactions under pressure is characterized by the use of complex catalysts, frequently mixtures.

In connection with other work a study of the decomposition of ethyl alcohol and ethyl alcohol-water solutions in the vapor phase over mixtures of catalysts was desirable. This paper contains the results obtained with a large variety of binary mixtures, and a few supported and promoted mixtures, of nickel and chromium. The effects of composition, methods of preparation and reduction procedures have been investigated and discussed.

Literature Review

Before examination of the present results it may be well to consider some of the more evident properties of the two individual catalysts. In general nickel

is a very active, but sensitive, dehydrogenating catalyst. Chromium, while not as active as nickel, is comparatively resistant to deactivation by harsh treatment. The reaction over chromium may vary from 40 to 90% dehydrating (10) depending upon the method of preparation.

The dehydrogenating action of nickel is well known and its action upon ethyl alcohol has been reported frequently. Sabatier and Senderens (19) observed that reduced nickel acted violently at relatively low temperatures to produce hydrogen and acetaldehyde. Beginning at about 150° C. the reaction was rapid and at 178° C. the gaseous products were 23% carbon monoxide, 29% methane and 48% hydrogen, the two former products being produced by the decomposition of acetaldehyde with subsequent hydrogenation of some of the carbon monoxide to methane. At temperatures about 50° C. higher the decomposition of carbon monoxide commenced and increased rapidly until, at a temperature of 330° C., the gas consisted of 19.5% carbon dioxide, 60.7% methane and 19.8% hydrogen.

Mond, Langer and Quincke (11) studied the variation in activity of different forms of nickel and found that the massive metal was less active than metal reduced from the oxide. The decomposition of carbon monoxide on massive nickel was not promoted until a temperature of 350° C. was reached. Adkins and Lazier (1) noted a variation in the activity of reduced nickel catalysts depending upon the nature of the reducing agent employed. Catalysts reduced with ethyl alcohol at 350°-420° C. were more active than similarly prepared samples reduced with hydrogen at 300°-400° C. These experimental results indicate quite clearly the activity of nickel in the catalytic decomposition of ethyl alcohol and show its marked dehydrogenating action.

The action of chromium has not been investigated to the same degree, but it is known that most non-reducible oxides are mixed catalysts promoting both dehydration and dehydrogenation at the same time. Sabatier and Mailhe (16) mention that Cr_2O_3 is a mixed catalyst promoting reactions with the simultaneous formation of ethylene, water, hydrogen and acetaldehyde. These workers also found that the crystallized oxide produced no gas at 350° C. and only a very small quantity of pure hydrogen at 400° C. (17). Lemoine (10) investigated the action of chromium catalysts on ethyl alcohol in more detail and found that the sesquioxide, prepared by dehydrating the blue precipitated hydroxide, produced a gas containing 91% ethylene and that after calcination at 500° C. this same oxide produced only 40% ethylene. Sabatier (15) concluded that the only form of chromium suitable for the dehydration of ethyl alcohol is the sesquioxide obtained by drying the precipitated hydroxide below 350° C. Calcination of the oxide resulted in a catalyst of equal dehydrating and dehydrogenating power. In the light of these results it follows that the dehydrating action of chromic oxide is pronounced and ought to be evident even in the presence of another powerful catalyst of different action.

The effect of water upon the decomposition of alcohol has also been investigated. Armstrong and Hilditch (3) using a copper catalyst found that the presence of water inhibited the decomposition of the aldehyde produced.

Hoover and Rideal (6) observed that water had a marked effect upon the ratio of dehydrating and dehydrogenating activity at the surface of a thoria catalyst. Lazier and Adkins (9) noted that water increased the carbon dioxide and hydrogen percentages in the gases produced. In a more recent paper Russell and Marschner (14) concluded that the presence of water increases the amount of alcohol decomposed and decreases the secondary decomposition of the aldehyde.

Discussion

In regard to the action of nickel and chromium mixtures, as shown by the present work, it may be said at once that the promoter action is slight or absent altogether. In general the mixtures behave as two chemical individuals, each having its characteristic properties modified by their relative concentrations and by the method of preparation. The effects due to the mixture as such are confined largely to the reactions subsequent to the initial decompositions. The relative activity of the two catalysts is easily determined and is of interest inasmuch as single catalysts may be classified by comparison of the actions of the different pairs of catalysts containing a common constituent. For example, it has been shown (5) in the case of a catalyst containing copper and chromium on silica, that the action of the chromium was greater than that of the copper at low temperatures, but as the temperature increased, the copper became more active relative to the chromium. The work reported here indicates that nickel is more active than chromium, but with vigorous treatment the relative activity of the two catalysts is shifted in favor of the chromium. From these results the apparent order of resistance of catalysts to thermal deactivation is, copper, chromium, nickel. This conclusion is verified to some extent by results which indicate that the depressing effect of water on the decomposition of alcohol is not as marked over nickel and chromium mixtures as Armstrong and Hilditch (3) found to be the case with copper.

The change in properties of catalysts with change in reaction temperature is of common occurrence and is evident in these mixed catalysts, there being a well-defined temperature region in which a marked change in the reactions occurs. This may be due to a change in the activity of the nickel or to a new effect which can be attributed to a mixture of the catalysts as a whole. The dehydrating action of the chromium is always evident and no abrupt change is apparent in this reaction.

Preparation of Catalysts

The present study involved the examination of the action of 20 catalysts. They varied in composition and in method of preparation as described below.

Catalyst No. 38 was prepared by the precipitation of nickel chromate from a nickel nitrate solution by potassium chromate. The nickel chromate was washed free of electrolytes and dried at 110° C.

Catalyst No. 46 was an equimolar mixture of c.p. samples of nickelous oxide and chromic oxide, wetted with water, ground, and dried at 110° C.

Catalyst No. 49 was prepared from the hydroxides of nickel and chromium precipitated together from an equimolar solution of the nitrates with sodium

hydroxide. The washed precipitate was dried, pulverized, triturated with water and dried at 110° C.

Catalysts Nos. 51 to 57 were prepared from nickel and chromium hydroxides precipitated with sodium hydroxide from the nitrates. The washed hydroxides were mixed wet in various proportions, dried at 110° C. and analyzed. The series contained the following percentages of nickelic oxide: 97, 86, 80, 66, 50, 40 and 9.

Catalyst No. 58 was prepared by the method used for Nos. 51-57 but with the substitution of ammonium hydroxide for sodium hydroxide. This catalyst was 53% nickelic oxide.

Catalyst No. 59 was pure chromic oxide prepared by precipitation of chromic hydroxide by potassium hydroxide from a solution of chromic nitrate. The precipitate was washed thoroughly and dried at 110° C.

Catalyst No. 60 was pure nickelic oxide prepared by the method used for catalyst No. 59 with the substitution of nickelic nitrate for chromic nitrate.

Catalyst No. 61 was prepared by soaking long fibre asbestos in an equimolar solution of the nitrates followed by ignition at 1000° C.

Catalyst No. 62 was prepared by evaporating an equimolar solution of nickel and chromium nitrates to dryness and igniting the resulting mass at 1000° C.

Catalysts Nos. 63 and 65 were prepared on porcelain chips by soaking them in an equimolar solution of the nitrates with subsequent boiling in potassium hydroxide solution. Catalyst No. 63 was drained and dried at 110° C. It contained potassium hydroxide as well as nickel and chromium oxides. Catalyst No. 65 was washed thoroughly to remove electrolytes and dried.

Catalyst No. 67 was prepared as in the case of No. 61 with the substitution of porcelain chips for asbestos.

Catalyst No. 68 was prepared by soaking an alumina gel in a solution of nickel and chromium nitrates and dried by ignition.

Catalyst No. 69 was prepared by treating alumina gel, that had been soaked in a solution of nickel and chromium nitrates, with potassium hydroxide solution. This mixture was filtered, washed and dried.

All catalysts, except where noted in the discussion, received the same treatment. They were subjected to the action of a slow stream of hydrogen for five to six hours at 300°-310° C.

Procedure

A standard apparatus as previously described (5) was used in this work. The alcohol solution was forced from a calibrated reservoir into a vaporizer at 105°-115° C. The vapors were led over the catalyst and the products removed rapidly through a capillary tube. Two condensers were used, the first at 10° C. and the second below 0° C. The total gas yield was measured by a wet test-meter and calibrated flow-meters gave instantaneous rate readings. Temperatures were determined by means of a noble-metal thermocouple placed in a glass well in the centre of the catalyst space. The interior and exterior of the catalyst tube differed in temperature by about 5° C. Gases were sampled over glycerol and analyzed in the usual manner with a Bureau of

Mines apparatus using copper oxide for carbon monoxide and hydrogen and slow combustion in oxygen for methane and ethane.

Unless otherwise stated the rate at which the alcohol solution passed into the catalyst chamber was 0.75 cc. per min. In case of 100% dehydrogenation this would correspond to about 225 cc. of hydrogen per min. with equal amounts of carbon monoxide and methane in the event of complete decomposition of the acetaldehyde produced in the primary reaction. The same figure represents the ethylene in case of dehydration. Any action due to water is not considered.

In view of the fact that an investigation of the gaseous products was the primary object of this work, the liquid products were not thoroughly examined. With these catalysts the liquids were complex mixtures of water, aldehydes, acids and esters. A complete and quantitative analysis was not made.

In the tabulated results the column showing the ratio liquid in/out, refers to the total liquid volumes concerned and in some cases the figure obtained is the result of several experiments.

Results

Of the great number of experiments performed, many were in relation to other investigations. Only those results having direct bearing on the subject under discussion will be presented.

Inspection of the data in Table I shows that in general the series of catalysts Nos. 51 to 57 gave the expected results. The nickel was much more active than the chromium, which is the reverse of the effect of copper in copper-chromium catalysts (5).

Catalyst No. 56 containing 97% of nickelic oxide indicated its activity by a sudden increase in temperature from 300° to 340° C. when the vapor reached it.

The gas yield varied with different conditions as shown in the table. As the temperature was raised, the activity as measured by gas flow reached a maximum at 300° C. and decreased above that temperature. A second run was started at 260° C. and in general the gas was richer in carbon dioxide, hydrogen and carbon monoxide and had a lower methane content. The rate of flow was larger and the temperature of maximum activity rose to 350° C. There is an abrupt change in the gas
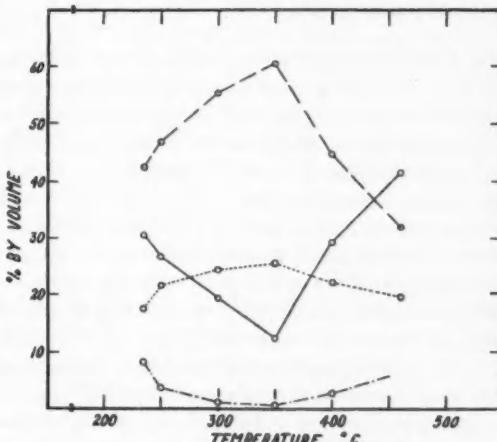
FIG. 1. *Results obtained with catalyst No. 53. Legend—composition of off-gases:* ——— H_2, — — CH_4, ····· CO_2, —·—· CO.

composition at this temperature of maximum activity which would point to some change in the nature of the catalytic action. The gas composition as plotted in Fig. 2 for this catalyst shows graphically the extent of the change. The production of hydrogen increases rapidly and may be due to the entry of water into the reaction. Carbon was deposited on the catalyst at all temperatures and there was always an excess of carbon dioxide over that expected from the amount of methane present. The protective action of water with copper catalysts (3) which prevents secondary decompositions is not apparent here. The dehydrating power of chromium is almost completely suppressed in the presence of so much nickel.
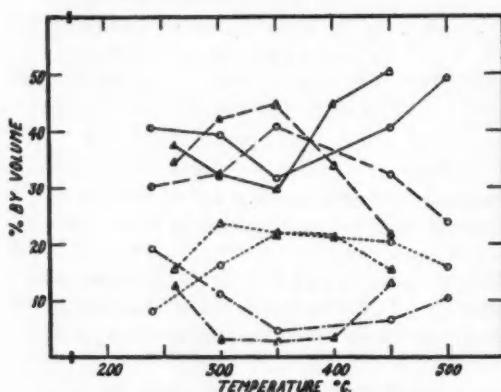
FIG. 2. *Comparison of results obtained with catalysts Nos. 52 (O) and 56 (△). Legend— composition of off-gases: as in Fig. 1.*

The results with catalyst No. 51 containing 86% of nickelic oxide were very similar to those obtained with catalyst No. 56. The change in the nature of the reaction occurred at 350° C. and carbon was deposited on the catalyst at all temperatures. This carbon was very reactive and easily removed by oxidation in a stream of oxygen at 300° C. The catalyst was again reduced with hydrogen and its activity examined. As shown in Table I this treatment altered the catalyst greatly resulting in very slight activity below 350° C. The change in the nature of the reaction occurred at 400° C. and was very slight. With rising temperature a maximum occurred in the production of carbon monoxide instead of a minimum, as shown by other catalysts, and the excess of carbon dioxide was even greater.

Catalysts Nos. 52 and 53 containing 80 and 66% of nickelic oxide respectively, were quite similar in their action to No. 56. The temperature at which the reaction altered was 350° C. Since these were both initial runs they seem to show an increase in this temperature with increasing chromium content. Both catalysts were heavily carbonized. They were less active at lower temperatures than those containing less chromium but were equally as good or better at higher temperatures. Figs. 1 and 2 show graphically the variation of gas composition with temperature and illustrate the change in the nature of the reaction in the region of 350° C.

Catalyst No. 54 with 50% of each oxide behaved quite differently from those preceding it. Although an abrupt temperature rise occurred when the alcohol reached the catalyst, the gas flow was small and intermittent at lower temperatures. Slight increases were noted in the percentage of methane and

oxides of carbon in the gas. It was also evident from the slight ethylene production that the dehydrating action of chromium was still very much in abeyance.

Catalyst No. 55, containing 40% of nickel and 60% of chromium oxides, was slightly less active than No. 54 but the gas analyses were very similar except at the higher temperatures. At 400° C. with a flow of 300 cc. per min. the decomposition of acetaldehyde was not as complex as usual nor was carbon formed to any great extent. Confirmation was clearly shown by the gas analysis. The yield of ethylene was surprisingly low and as before became smaller with rising temperature.

Catalyst No. 57, containing only 9% of nickelic oxide, was much less active than any in this series, producing a gas flow of only 20 cc. per min. at 325° C. and 40 cc. per min. at 400° C. Practically no carbon was formed on this catalyst. The dehydrating action of the chromium was becoming apparent although not to the extent that might be expected.

Another catalyst that should be considered with this series is No. 58, which contained 53% of nickelic oxide and was prepared with ammonium hydroxide as precipitant. The results are not tabulated since they correspond very closely to those obtained with catalyst No. 54. They illustrate, in this case, the fact that the properties of the catalyst are independent of the precipitating agent.

The dehydrating action of the chromium having been so thoroughly depressed, it was thought that the ultimate form of the chromic oxide might have been one of those mentioned by Sabatier (15) as essentially dehydrogenating. Catalyst No. 59 of pure precipitated chromic oxide partially verified this conclusion. As shown in Table II, at 340° C. the catalyst behaved about 25% as a dehydrating agent and 75% as a dehydrogenating agent. At 420° C. the gas analysis showed the reaction to be approximately 40% dehydration and 60% dehydrogenation. It was noted previously that the yield of ethylene decreased with rising temperature in the mixed catalysts but in this case the reverse is true. This would indicate that in the mixed catalysts described, the activity of the nickel increases more rapidly with temperature than does the activity of the chromium. The negligible production of carbon monoxide and carbon on this catalyst would suggest that the principal secondary reaction was the formation of liquid products and carbon dioxide from acetaldehyde.

Catalyst No. 60, of pure nickel, was examined in order to throw light on the total effect of the chromium in the mixed catalysts. The results of this series of runs are shown in Table II. The catalyst was carbonized and the gas analysis would suggest a fairly consistent and large decomposition of carbon monoxide to carbon dioxide. These results are very much as expected. showing an action at least 98% dehydrogenation. The higher the temperature the greater was the decomposition of the acetaldehyde. Due to secondary reactions there was a small excess of carbon dioxide over that to be expected from the decomposition of the carbon monoxide. It was noted that the catalyst was very sensitive and lost its activity rapidly. Subsequent runs to those shown in Table II gave gas flows of the order of one-half the tabulated values.

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TABLE I

RESULTS OBTAINED ON PASSING ETHYL ALCOHOL VAPOR OVER VARIOUS MIXED CATALYSTS

Temp., °C.	Liquid flow, cc./min.	Composition of gas, % by vol.					Gas flow, cc./min.	Ratio liquid in/out
		CO_2	H_2	C_2H_4	CH_4	CO		
Catalyst No. 51; 86% nickelic oxide, after oxidation and reduction.								
450	0.75	17.1	58.5	nil	16.3	8.3	450	
410		15.7	44.4	0.7	27.1	12.1	300	
350		15.4	58.8	1.5	15.1	9.1	150	
Catalyst No. 52; 80% nickelic oxide.								
240	0.75	8.3	40.8	1.4	30.2	19.5	220	
300		16.4	39.4	0.5	32.4	11.3	600	1.5
350		22.0	31.8	0.5	40.9	4.7	800	
450		20.4	40.4	0.4	32.1	6.8	800	
500		16.0	49.3	0.4	23.9	10.4	800	4.8
Catalyst No. 53; 66% nickelic oxide.								
235	0.75	17.6	30.6	1.1	42.5	8.3	350	
250		21.6	26.8	0.9	46.8	3.9	500	
300		24.1	19.4	0.4	55.3	1.1	525	3.6
350		25.5	12.6	0.8	60.3	0.8	550	
400		22.0	29.2	0.4	44.7	2.9	600	
460		19.5	41.5	0.6	32.0	6.5	600	4.8
Catalyst No. 54; 50% nickelic oxide.								
280	0.75	9.1	39.4	1.1	33.2	17.2	150	
385		4.7	41.3	nil	31.2	22.9	320	
Catalyst No. 55; 40% nickelic oxide.								
350	0.75	2.5	69.5	1.1	20.8	6.0	120	
400		1.8	51.7	nil	24.1	22.3	320	
Catalyst No. 56; 97% nickelic oxide.								
First run								
235	0.75	16.6	39.0	0.7	33.9	9.9	400	
265		23.5	25.4	0.8	48.1	2.3	425	
300		24.4	17.8	0.4	57.0	0.6	600	
325		24.3	29.0	0.6	43.8	2.4	500	
350		23.1	30.9	0.6	43.1	2.2	450	2.4
Second run								
260	0.75	15.9	37.8	0.2	34.4	11.8	425	
300		23.7	32.2	0.8	42.1	3.0	600	
350		22.1	29.9	0.6	44.6	2.9	700	
400		21.5	44.8	0.2	33.9	3.4	525	
450		15.4	50.3	0.8	21.7	13.0	500	3.9
Catalyst No. 57; 9% nickelic oxide.								
400	0.75	3.6	64.7	4.6	14.0	13.2	40	

TABLE II

RESULTS OBTAINED ON PASSING ETHYL ALCOHOL VAPOR OVER SINGLE CATALYSTS

Temp., °C.	Liquid flow, cc./min.	Composition of gas, % by vol.					Gas flow, cc./min.	Ratio liquid in/out
		CO₂	H₂	C₂H₄	CH₄	CO		
Catalyst No. 59; pure precipitated chromic oxide.								
340	0.75	5.5	54.4	18.0	20.7	1.4	340	
420		8.7	51.0	30.4	8.2	nil	500	1.1
Catalyst No. 60; pure precipitated nickelic oxide.								
270	0.75	14.7	49.9	1.1	23.0	11.4	180	
285		21.2	52.8	1.0	20.1	4.8	375	
300		20.6	53.4	0.8	20.6	4.6	425	
350		21.2	42.8	0.6	29.2	6.2	500	
400		20.3	43.8	nil	30.5	5.5	500	2.2

The difference in catalytic activity of the simple and the mixed catalysts is well illustrated by a comparison of the results in Tables I and II. With the mixed catalysts, there were certain ranges of temperature in which a decided change in catalytic action and possibly catalyst surface occurred. The quantities of carbon dioxide and methane reach their maxima at this temperature on the mixed catalyst, while with the single catalysts they are at a minimum. The production of hydrogen reaches a minimum on the mixed catalysts and a maximum on the single catalysts in the same temperature range. This would indicate a more simple reaction on the single catalysts, involving to a large extent only decomposition of acetaldehyde subsequent to dehydrogenation.

The structure of a catalyst is conceded to have an important influence upon its activity (2). That these mixtures of catalysts are no exception to this rule is evident from the results with catalysts Nos. 46, 49 and 62, given in Table III. These catalysts all contained the same percentages of nickel and chromium but were prepared by different methods and received widely different treatments.

With catalyst No. 49, prepared by precipitation, it will be observed that the results are roughly similar to those previously described and shown in Table I. It should be noted however that there were relatively large amounts of carbon monoxide in these gases when compared with those of Table I, and that there was an increase in the ethylene production showing enhancement of the activity of the chromium. Less carbon monoxide was decomposed pointing to a reduction in the activity of the nickel. The catalyst lost some of its activity at 425° C. as was evident from the decreasing gas yield and increasing hydrogen concentration. A second run at 230° C. gave only 70 cc. of gas per min. The reduction in activity was probably due to the decrease in active surface by carbon deposition, as the gas analyses were the same with both runs at 230° C.

As might be expected, catalyst No. 46 was less active than the corresponding catalysts of Table I prepared from freshly precipitated hydroxides. The action started at 350° C. with a gas flow of 200 cc. per min. and dropped rapidly to a few cc. per min. At 450° C. only 55 cc. of gas was produced per min. Ethylene was present in appreciable quantities that increased with temperature. The catalyst was largely a dehydrogenation type and caused little secondary decomposition.

A portion of this same catalyst was reduced with pure alcohol instead of hydrogen. The catalyst was very much more active and contrasted strongly with the other sample. This was in accord with the results of Adkins and Lazier (1) which showed the influence of the reducing agent on the activity of the catalyst. Table III gives the results of two runs. In spite of carbon deposition during reduction and from the subsequent experimental runs, the gas flow was quite appreciable. The decomposition was comparatively simple and consisted of dehydrogenation followed by aldehyde decomposition. The percentage of ethylene was slightly less, showing that the effect of the alcohol reduction process is largely on the nickel.

Catalyst No. 62 of the ignited series was very inactive. The action of the chromium was more apparent in this catalyst and would indicate the greater sensitivity of nickel to harsh treatment.

TABLE III

THE EFFECT OF VARIOUS METHODS OF PREPARATION ON THE SAME CATALYST

Temp., °C.	Liquid flow, cc./min.	Composition of gas, % by vol.					Gas flow, cc./min.	Ratio liquid in/out
		CO_2	H_2	C_2H_4	CH_4	CO		
Catalyst No. 46; equimolar mixture of nickelous oxide and chromic oxide.								
350	0.75	6.9	78.7	2.4	8.5	3.5	slight	1.1
450		8.1	72.9	3.6	11.4	4.1	55	1.2
Same reduced with alcohol								
350	0.75	0.4	62.0	1.1	17.6	18.9	150	1.3
450		9.3	45.7	2.0	23.7	19.4	300	1.9
Catalyst No. 49; equimolar mixture of precipitated hydroxides of nickel and chromium.								
230	0.75	5.2	54.1	0.9	23.9	16.0	200	1.2
300		11.3	44.4	1.5	23.3	19.4	320	1.6
350		16.8	43.0	4.0	25.9	11.9	420	1.6
400		15.5	45.0	2.9	25.1	12.2	600	2.2
425		16.4	56.8	2.0	18.3	6.1	400	
Catalyst No. 62; equimolar mixture of nickel and chromium nitrates ignited at 1000° C.								
450	0.75	1.3	66.0	13.4	12.7	6.5	70	1.6

As shown in Table IV, catalyst No. 61 of the ignited series on supporting material was inactive even when compared with catalyst No. 62 which was

not supported.   Catalyst No. 67 of the same type showed very similar results. The gas flow was very small with only a slight secondary decomposition of acetaldehyde.   The activity of the chromium was again decreased.

The inactivity of ignited catalysts was not unexpected in view of the work of Taylor and Burns reported by Bancroft (4) and Gilfillan (8), but more than this, it was found with these mixed catalysts that the constituents were affected in widely varying degree.   Supported catalysts frequently show an increased activity (7) but with the examples investigated the reverse was more nearly true.   The unsupported mixed catalysts did not behave as though each metal were exerting its influence altogether independent of the other.   The supported catalysts, however, retained only a portion of the activity of the individuals and on ignition lost all but a slight activity.   Although very inactive they showed that two distinct primary reactions occurred, indicating that the catalyst was to some extent a mixture of two independent catalysts. The very common secondary reaction involving the formation of carbon dioxide and carbon from carbon monoxide did not occur on these catalysts.

Catalyst No. 63 using porcelain as a support for the precipitated oxides was comparatively inactive though not as unsatisfactory as the ignited series.   The gas flows were 10, 20 and 25 cc. per min. at 350°, 450° and 500° C. respectively, and no carbon was deposited.   The composition of the gas was independent of temperature and only one analysis is given in Table IV.

Catalyst No. 65, which was similar to No. 63 except that it was free from alkali, appeared slightly more active, and it will also be noticed that there was a great deal more ethylene produced or surviving in the presence of the excess alkali.

Attempts to activate these two catalysts met with no success.   The small gas yields were contrary to expectation and might be explained on the basis of a smaller available surface.   The gas analyses were so different from those obtained with catalysts Nos. 49 to 58 that the use of a supporting material must be considered as a fundamental alteration in the catalyst.

In the case of the catalysts supported on alumina, No. 68, prepared by ignition, was entirely inactive up to 400° C. and was not investigated further. Catalyst No. 69, prepared by precipitation, was much more active as shown in Table IV.   Here again the support seemed to have altered the nature of the decomposition reactions appreciably.

The last in this series of mixed nickel and chromium oxides was No. 38 with the theoretical composition of nickel chromate.   The first runs were made on a carbonized sample from previous work with alcohol mixtures.   As shown in Table V action commenced at about 300° C. and the gas yield increased steadily with rising temperature.

A fresh sample of the same catalyst, after reduction with hydrogen for six hours, gave the results indicated.   It will be noticed that on this more active catalyst, the ethylene production was decreased and the carbon dioxide was increased, the latter probably at the expense of the carbon monoxide.   From the low hydrogen production it was evident that some hydrogenation of the carbon oxides occurred.

TABLE IV

EFFECT OF THE SUPPORTING MEDIUM ON THE ACTION OF CATALYSTS

Temp., °C.	Liquid flow, cc./min.	Gas composition, % by vol.					Gas flow, cc./min.	Ratio liquid in/out
		CO_2	H_2	C_2H_4	CH_4	CO		

Catalyst No. 61; equimolar solution of nickel and chromium nitrates ignited on asbestos.

Temp., °C.	Liquid flow, cc./min.	CO_2	H_2	C_2H_4	CH_4	CO	Gas flow, cc./min.	Ratio liquid in/out
450	0.75	1.8	87.0	4.4	6.2	0.6	35	1.2

Catalyst No. 63; equimolar mixture of nickel and chromium hydroxides precipitated on porcelain with boiling KOH and drained.

| 450 | 0.75 | 2.2 | 86.7 | 5.4 | 4.7 | 1.0 | 20 | 1.2 |

Catalyst No. 65; same as No. 63 with the excess alkali washed out.

| 450 | 0.75 | 1.0 | 82.0 | 10.0 | 5.5 | 1.5 | 35 | |

Catalyst No. 69; equimolar solution of nickel and chromium nitrates precipitated on fresh alumina gel with hot KOH.

| 325 | 0.75 | 2.3 | 72.0 | 5.0 | 7.7 | 13.0 | 90 | |
| 400 | | 2.8 | 64.1 | 7.7 | 15.0 | 10.3 | 210 | |

Another new sample of the catalyst was reduced with hydrogen for four hours. The solution used in this set of experiments was 34 mole per cent alcohol. The results as shown in Table V are very similar to those given with the previous sample for the equimolar solution and would suggest that the water is not entering into the reaction.

The same sample of catalyst was treated with oxygen at 300° C. to remove the carbon deposit. The carbon was very active, being converted rapidly to carbon dioxide at this temperature although it is probable that the actual temperature on the catalyst was greater than 300° C. After reduction with hydrogen, equimolar alcohol solution was passed over the catalyst. It will be noticed that the ethylene production was low, indicating that the effectiveness of the nickel had not been impaired relative to the chromium.

The action of prolonged reduction with hydrogen is of interest in the way the decomposition of carbon monoxide was affected. A used portion of catalyst No. 38 was oxidized and then reduced with hydrogen for 15 hr. at 300° C. This catalyst was less active than those reduced for a shorter time, as the catalyst showed no activity below 350° C. The gas composition shows the secondary decomposition of carbon monoxide to carbon dioxide to be comparatively slight.

A second portion of used catalyst was oxidized and then reduced with carbon monoxide. There was no formation of carbon on the catalyst during reduction. With alcohol solution the catalyst was very inactive with no reaction below 400° C.

A new sample of catalyst No. 38 was reduced at 295° C. with pure alcohol.

No carbonization of the catalyst occurred. This catalyst verified further the findings of Adkins and Lazier (1) on the influence of reducing agents. As shown in Table V, the catalyst reduced with alcohol was more active than that reduced with hydrogen and carbon did not form on the catalyst until the temperature was above 350° C. It has already been shown that catalyst No. 46 was also more active after reduction with alcohol than after hydrogen treatment, thus emphasizing the effect of the method of reduction on activity.

The temperature at which carbon deposition occurred corresponded approximately with the abrupt change in the nature of the reaction between 375° and

TABLE V

EFFECT OF VARIOUS TREATMENTS UPON CATALYST No. 38, NICKEL CHROMATE

Temp., °C.	Liquid flow, cc./min.	Gas composition, % by vol.					Gas flow, cc./min.	Ratio liquid in/out
		CO_2	H_2	C_2H_4	CH_4	CO		
Sample used in previous work.								
300	0.55	7.4	46.0	1.3	23.4	21.7	100	1.1
350		7.5	49.5	0.8	22.0	20.2	300	1.3
400		18.2	40.5	0.2	35.0	6.2	420	
Fresh sample.								
350	0.55	23.8	34.2	nil	38.3	3.7	420	3.5
450		23.2	32.7	0.8	42.2	1.1	280	4.4
Solution used containing 66% water.								
300	0.65	17.8	36.9	0.7	37.2	7.4	350	
350		20.5	27.8	0.4	47.9	5.4	400	
400		19.9	40.5	1.1	31.8	6.9	550	1.8
Above catalyst oxidized and reduced, re-run with equimolar alcohol and water.								
350	0.65	14.2	51.9	0.2	22.2	11.3	80	1.8
Oxidized and reduced with hydrogen for 15 hr.								
350	0.65	3.4	61.6	2.0	14.9	18.0	50	
400		7.1	47.5	0.7	25.4	19.3	270	3.2
Reduced with carbon monoxide.								
500	0.65	18.2	40.5	0.2	35.0	6.2	350	4.0
Reduced with ethyl alcohol.								
300	0.50	5.9	62.6	2.8	17.3	11.4	25	1.1
350		3.3	66.0	1.6	13.9	15.2	50	1.2
375		3.8	45.5	1.6	25.2	23.9	120	1.4
400		23.3	27.4	0.5	44.9	4.1	250	5.0
425		23.2	28.4	0.4	44.2	3.8	200	5.2

400° C. but there is no apparent relation to the action of the series 51 to 57. As in the results reported on other samples of catalyst No. 38, secondary decompositions occurred almost exclusively with carbon monoxide. A blank experiment carried out with active carbon in place of a metallic catalyst showed carbon to be relatively inactive. The abrupt change as shown was evidently a temperature effect.

Summary

A large amount of data has been secured which is rather difficult to interpret completely without analysis of the liquid products. Nevertheless certain conclusions may be stated. In mixed catalysts of the type described, the activity and the nature of the reactions generally depended largely on the method of preparation. The activity of the chromium was not evident unless the catalyst had undergone severe treatment. Nickel was much more sensitive to vigorous treatment than chromium.

A variety of reactions is possible and apparently the number and nature of the reactions that occurred were functions not only of the history of the catalyst, but also of the temperature. The nature of the reducing agent used in preparing the catalyst was of importance, at least in two cases investigated, in determining the course of secondary reactions.

Generally, the most active catalysts for the primary reaction also promoted the secondary reactions. A possible exception to this rule was found in nickel chromate which would have a distinctly different structure from catalysts of the mixed oxide type. In all catalysts the dehydrating power of chromium was largely suppressed by the presence of nickel.

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STUDIES ON THE ACTION OF SULPHATES ON PORTLAND CEMENT

IV. THE ACTION OF SULPHATE SOLUTIONS ON MORTARS PREPARED FROM SOME BINARY AND TERNARY COMPOUNDS OF LIME, SILICA, ALUMINA AND IRON[1]

By T. Thorvaldson[2], D. Wolochow[3] and V. A. Vigfusson[4]

Abstract

A study was made of the action of solutions of the sulphates of magnesium, sodium and calcium on 1:10 mortar prisms. The prisms were made with standard sand and the following substances or mixtures of these: tricalcium silicate, β-dicalcium silicate, γ-dicalcium silicate, tricalcium aluminate, $5CaO.3Al_2O_3$, monocalcium aluminate, $3CaO.5Al_2O_3$, dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$. Some of the experiments dealt with mortars of richer mix (1:7½ and 1:5). The effect of the solutions was determined by measuring the linear expansion of the prisms and the tensile strength when the measurements of expansion were discontinued. A very pronounced difference was found to exist between the behavior of mortars made with mixtures rich in tricalcium silicate and those rich in β-dicalcium silicate. This observation is applied in the discussion of the resistance of the different types of hydraulic cements to the action of sulphate solutions.

Introduction

The scientific literature dealing with the disintegration of Portland cement when exposed to sulphate-bearing waters, such as sea water, mine waters, and the so-called "alkali" water, has reached very large proportions. Studies have been reported dealing with the action of these waters on both unhydrated and hydrated cement, on mortar and concrete specimens in the laboratory and in the field, and on concrete structures such as aqueducts, dams and docks. This literature contains reports of many apparently conflicting observations as to the permanence of well-made concrete, the relative harmfulness of the different sulphates or other salts which may be present in these waters, and the effects produced by varying the conditions of manufacture or curing of the concrete.

One of the obvious reasons for such inconsistencies is the fact that the most important basic material, the hydraulic cement, though conforming to certain specifications as to physical properties and falling within certain rather indefinite limits as to chemical composition, is in reality a highly variable material, considered from the standpoint of the actual chemical compounds present.

To illustrate this, one might consider the composition of, say, three commercial Portland cements which passed the standard specifications for all the physical requirements and gave on chemical analysis the results shown in Table I.

A comparison of these analyses with the range of values given by Eckel (4) for American Portland cements is given in Table II.

TABLE I

Composition of three Portland cements

Cement No.	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %	Ign. loss %	Free CaO %
1	20.02	6.97	2.61	63.48	3.86	1.85	1.25	0.10
2	22.00	8.06	2.87	60.95	2.86	2.02	1.28	0.03
3	22.56	6.06	4.36	61.67	2.66	1.53	1.00	0.00

TABLE II

Variation in composition of American Portland cements

	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	CaO %	MgO %	SO_3 %
Eckel (4)	19.06–24.48	4.51–11.11	1.61–5.18	58.07–65.44	0.25–3.53	0.25–2.86
Cements Nos. 1, 2 and 3	20.02–22.56	6.06–8.06	2.61–4.36	60.97–63.48	2.66–3.86	1.53–2.02

It will be seen that the three Portland cements of Table I are of very uniform composition as compared with the American cements for which the analyses are given by Eckel. In no case does the percentage of lime, silica, alumina or iron oxide fall anywhere near the extreme values given, and the range between the highest and lowest value is in each case less than one-half of that given for commercial Portland cements of American manufacture. If one accepts in general the statement so often made, to the effect that commercial Portland cements are of very uniform chemical composition, then this would be doubly true of cements Nos. 1, 2, and 3 above.

When these three cements are made into mortar or concrete test pieces and exposed to fresh water, their behavior is very similar, but when exposed to water containing sulphates their behavior shows extreme differences. The chemical analyses as expressed above do not suggest a reason for this difference, but if one calculates the percentage of each of the chemical compounds present on the assumption that equilibrium had been attained during burning (the low percentage of free lime indicates that equilibrium had been attained) one is no longer astonished that there might be a difference in behavior when exposed to

TABLE III

Calculated compounds present in cements of Table I

Cement No.	Percentage of compounds						
	Free lime	Tricalcium silicate	Dicalcium silicate	Tricalcium aluminate	$4CaO.Al_2O_3.Fe_2O_3$	Calcium sulphate	Magnesium oxide
1	0.10	50.0	19.7	14.05	7.94	3.15	3.86
2	0.03	16.8	50.4	16.51	8.73	3.43	2.86
3	0.00	28.3	43.3	8.67	13.30	2.60	2.66

aggressive waters. The results of such a calculation by the method of Colony (3) as modified by Bogue (2) are given in Table III.

It is thus seen that the percentages of the four most important compounds present vary greatly: tricalcium silicate from 16.8 to 50.0%, dicalcium silicate from 19.7 to 50.4%, tricalcium aluminate from 8.67 to 16.51%, $4CaO.Al_2O_3.Fe_2O_3$ from 7.94 to 13.30%. In view of the difference in the chemical properties of these compounds, one would expect great differences in the behavior of the different cements when attacked by corrosive solutions.

It is evident that a study of the reactions of sulphate solutions on the individual compounds present in hydraulic cements would be of primary importance in determining the material most resistant to the action of sulphate-bearing waters. The results of investigations of this kind have already been published, among these being the microscopic study by Shelton (13, 14, 15) in which he studied the action of sodium and magnesium sulphates on the substances, tricalcium silicate, β-dicalcium silicate and the four aluminates of calcium, both in the hydrated and the unhydrated form, and on a white Portland cement. Although such studies have given valuable information, their application to the disintegration of mortar or concrete in sulphate solutions presents difficulties.

Thorvaldson, Vigfusson and Larmour (18) studied the action of solutions of sodium, magnesium, and calcium sulphates on mortar bars made from pure tricalcium silicate, β-dicalcium silicate and tricalcium aluminate or mixtures of these mixed with standard sand (one part of silicate to five parts of sand by weight). The course of the action of the solution on the mortar bars was followed by means of accurate measurements of expansion. At the end of two years' exposure to solutions of sodium sulphate (2.2% and 8.1% of Na_2SO_4), under conditions which, in the case of similar specimens made from Portland cement, would have resulted in the initial indications of disintegration in from 5 to 10 days and complete failure in about one month, the specimens of mortar made from pure tricalcium silicate and β-dicalcium silicate showed no signs of being adversely affected. Exposure of mortar bars of the same composition to solutions of magnesium sulphate (1.9 and 6.8% of $MgSO_4$) caused slow expansion and ultimate disintegration, while similar bars, in which tricalcium aluminate to the extent of 25% of the amount of the silicate was present, expanded and disintegrated rapidly both in solutions of sodium sulphate and magnesium sulphate. A sand mortar made with a mixture of tricalcium silicate, β-dicalcium silicate, and tricalcium aluminate gave specimens which developed strength in a manner very similar to Portland cement and expanded and disintegrated very rapidly when exposed to solutions of the sulphates of sodium, magnesium and calcium, giving expansion-time curves which showed a somewhat more rapid expansion than similar bars made of Portland cement. The only marked difference observed was that the mortar made from the composite cement was not rendered as immune to the action of sulphates by curing in steam as similar specimens made from commercial Portland cement.

The experiments described in the present paper represent a more extensive

study of the same kind, including not only mortar specimens made with the compounds present in Portland cement, but also those present in high alumina and iron ore cements.

The value of expansion measurements as a means of following the progress of the disintegration of mortar and concrete specimens made from Portland cement and exposed to sulphate solutions has already been discussed by the authors (19). Not only is the expansion a measure of the stress which would be developed if the material was not free to expand, but it is also possible to predict from such measurements the loss in strength of the test pieces (10, 17). The application of the method to the prediction of loss of strength in the case of mortars prepared from cements, the composition of which does not fall within the limits for Portland cement, is not so certain. In the present series of experiments however, work is carried on under conditions which, for corresponding mixes of ordinary Portland cements, produce visible effects on the specimens in the course of a week or two and complete disintegration as a rule within one month. It is, therefore, evident that expansion measurements extending over three years' exposure combined with observations as to any visible physical effects, and, in many cases, determinations of tensile strength of the specimens, will in any case give fairly reliable evidence as to the resistance of the material being studied.

Preparation of Cement Substances*

The cement compounds were with slight modifications prepared according to the methods outlined by Rankin (11, 12), Bates and Klein (1), Lerch and Bogue (8) and Hansen, Brownmiller and Bogue (7). The raw materials used in the preparation were as follows: (1) White marble which on ignition gave a residue of 56.27% and which showed only traces of impurities present. (2) Flint which contained 98.45% of silica. (3) Hydrated alumina, a very pure sample containing 65.28% of alumina. (4) Ferric oxide, a c.p. sample of high purity. With the exception of the flint, which was much more finely ground, these materials were pulverized to pass a 200-mesh sieve, and were mixed very thoroughly in the required proportions before firing. Sufficient water was added to the mixed materials (in some cases coal oil was used) to enable them to be molded into hollow cylinders which were dried and then fired either in a compressed air-oil, or in a gas-fired, furnace until well sintered, the temperature being determined by a Leeds and Northrup optical pyrometer. The sintered material was then broken up, reground to pass a 200-mesh sieve and refired, this process being repeated as often as was necessary to obtain complete combination as shown by the absence of free lime, and by a uniform refractive index. A complete chemical analysis of the product was usually made as a further check before the final firing.

In the preparation of tricalcium silicate the initial mixture was of the composition $2CaO:SiO_2$. This was fired at about 1550°C. until the product contained no free lime and after dusting was composed almost entirely of

γ-dicalcium silicate. The extra mole of lime required to form tricalcium silicate was then added in three portions of 0.5, 0.25, and 0.25 mole, with intermediate firing at 1500° to 1580°C. After a final regrinding and firing for six hours at this temperature, the microscopic examination indicated a uniform product free from particles of lime, having a refractive index of 1.715. White's test (20) was negative and a determination of lime by the method of Emley as modified by Lerch and Bogue (9) also gave a negative result.

The preparation of γ-dicalcium silicate was similar to the first step in the production of tricalcium silicate, the fired cylinder being cooled very slowly to favor the inversion from the β- to the γ-form. Microscopic examination showed only γ-dicalcium silicate.

In the preparation of β-dicalcium silicate the main problem is the prevention of the inversion of the substance to the γ-form. Chromic oxide (0.5%) was added to the mix and the cylinder was quenched in cold water Even with this treatment the final sample contained small amounts of the γ-form.

The sample of tricalcium aluminate was prepared by repeated firing of the cylinder at a temperature of 1300° to 1400°C. It was found that addition of water to the finely ground material between firings hastened combination, probably on account of the hydration of any high-burned lime present in the material. Microscopic examination showed the presence of a very small amount of $5CaO.3Al_2O_3$ in the final sample. The other three aluminates were prepared by firing the required mixtures of calcium carbonate and hydrated alumina at temperatures somewhat below the melting points of the respective aluminates. None of the products contained any free lime. The monocalcium aluminate contained a slight trace of $5CaO.3Al_2O_3$ while the sample of $3CaO.5Al_2O_3$ was entirely homogeneous. The sample of dicalcium ferrite was fired for two periods of about two hours each at a temperature of 1150° to 1200°C. After the second firing the material was homogeneous. The compound $4CaO.Al_2O_3.Fe_2O_3$ was fired for two three-hour periods at about 1250°C. The final product was homogeneous and had the optical properties given by Hansen, Brownmiller and Bogue (7).

Preparation and Curing of Mortar Specimens

A summary of the composition of the "cements" used in the main series of experiments is presented in Table IV. The specimens used for the expansion measurements were mortar bars made from the single or mixed compounds and standard Ottawa sand (20-30 mesh), distilled water being used for obtaining a plastic mix. The proportion was, unless otherwise specified, 1 part of the compound or mixture of compounds to 10 parts of standard sand by weight. This is an extremely lean mix, so that the specimens were very permeable to the solutions and very rapid action was therefore to be expected. The specimens were made in collapsible steel frames so as to give rectangular prisms measuring 1.55 by 1.55 by 10 cm. A smooth end was obtained by means of a thin layer of neat cement made from the cementing substance used in each case. The molds were stored in the damp closet until the bars were strong enough to be removed without serious accidental breakage. Those containing

TABLE IV

COMPOSITION OF "CEMENTS" USED IN MAIN SERIES OF EXPERIMENTS (SERIES 101. 1:10 MORTARS)

Serial letter	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	ZZ
Batch No.	151	152	176	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	177	178	179	180	181	182	183	184	185
$3CaO.SiO_2$, %	100						80	80	80	80	80	80							50	40	40	40	40	40	40	40	40
$\beta\text{-}2CaO.SiO_2$, %		100											80	80	80	80	80	80	50	40	40	40	40	40	40	40	40
$\gamma\text{-}2CaO.SiO_2$, %			100																								
$3CaO.Al_2O_3$, %							20						20							20							
$5CaO.3Al_2O_3$, %				100				20						20							20					10	6.6
$CaO.Al_2O_3$, %					100				20						20							20				10	6.6
$3CaO.5Al_2O_3$, %						100				20						20							20				
$2CaO.Fe_2O_3$, %											20						20							20			
$4CaO.Al_2O_3.Fe_2O_3$, %												20						20							20		6.6
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
CaO, %	73.7	65.1	65.1	47.8	35.5	24.8	71.4	68.5	66.0	63.9	67.2	68.2	64.6	61.7	59.2	57.1	60.4	61.4	69.4	68.0	65.1	62.6	60.5	63.8	64.8	66.5	65.6
SiO_2, %	26.3	34.9	34.9	—	—	—	21.1	21.1	21.1	21.1	21.1	21.1	27.9	27.9	27.9	27.9	27.9	27.9	30.6	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5
Al_2O_3, %	—	—	—	52.2	64.5	75.2	7.5	10.4	12.9	15.0	—	4.2	7.5	10.4	12.9	15.0	—	4.2	—	7.5	10.4	12.9	15.0	—	4.2	9.0	6.5
Fe_2O_3, %	—	—	—	—	—	—	—	—	—	—	11.7	6.5	—	—	—	—	11.7	6.5	—	—	—	—	—	11.7	6.5	6.0	3.9
Total, %	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

80% or more of tricalcium silicate, or the three aluminates possessing marked hydraulic properties ($5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$) were removed in 20 days. They were then all in excellent condition except the batches containing dicalcium ferrite (161) and $4CaO.Al_2O_3.Fe_2O_3$ (162), which were weak. At that time the bars containing a large amount of β-dicalcium silicate were rather weak, so they were left in the molds for another two weeks. The bars containing the mixture of β-dicalcium silicate and dicalcium ferrite or $4CaO.Al_2O_3.Fe_2O_3$ (Batches 167-168) were still soft and even after a total curing time of seven weeks many broke on being removed from the molds. The bars made from γ-dicalcium silicate did not appear to set for several weeks but at the end of 10 weeks it was possible to remove them from the molds without excessive breakage. After removal from the molds the bars were placed in distilled water until eight weeks old, when they were exposed to the solutions. The only bars treated differently were those containing γ-dicalcium silicate and these were cured in water until five months old, and then exposed to the solutions.

Experimental Procedure

Three sulphate solutions were used in these experiments, namely 0.15 M Na_2SO_4 (2.1% by weight); $0.15M$ $MgSO_4$ (1.8% by weight); and a saturated solution of calcium sulphate. A few experiments were made with 0.5 M solutions of the first two salts. The solutions of sodium and magnesium sulphates were prepared from recrystallized salts and contained only traces of impurities. The solution of calcium sulphate was prepared from a pure sample of ground gypsum, a large excess of the gypsum powder being added to each jar of saturated solution and the solution thoroughly stirred from time to time. The bars were exposed to the sulphate solutions in pint glass jars which were tightly sealed except when measurements were being made. Duplicate bars were immersed in each jar containing 450 cc. of the solution.

Measurements of the lengths of the bars were made from time to time with a micrometer head set in a steel frame. The micrometer head was graduated to read to 0.01 mm. so that the lengths of the 10 cm. bars were determined to 1 part in 10,000 (0.01%). All the experimental work was carried on in constant temperature rooms at $21°C.$ ($70°F.$) The temperature of the solutions in the jars rarely varied more than $\pm 0.1°C.$ from this mean.

Experimental Results

I. Mortars of the Calcium Silicates and Sand

The solutions in which the mortar bars were immersed are indicated in Table V. The bars were composed of 1 part by weight of the silicate indicated and 10 parts of standard sand, 20-30 mesh. Each solution is always represented by the same numeral while the letter refers to the composition of the cementing substance as given in Table IV. The combined number and letter therefore identify the composition of the bar and of the solution in which it was immersed and will be used in the text to refer to the corresponding expansion-time curves which are all labelled in this manner.

TABLE V

EXPOSURE OF 1:10 MORTARS MADE FROM THE PURE SILICATES OF CALCIUM

Silicate	Solution				
	Na₂SO₄		MgSO₄		CaSO₄
	0.15M	0.50M	0.15M	0.50M	Saturated at 21° C.
3CaO.SiO₂	1A	3A	2A	4A	21A
β-2CaO.SiO₂	1B	3B	2B	4B	21B
γ-2CaO.SiO₂	1C	—	2C	—	21C
{50% 3CaO.SiO₂ {50% β-2CaO.SiO₂	1S	—	2S	—	21S

Expansion Curves for the Silicate Mortars in Solutions of Magnesium Sulphate

Fig. 1 shows the expansion-time curves for the experiments outlined in Table V. It will be seen that the 1:10 mortar bars made of tricalcium silicate, β-dicalcium silicate, γ-dicalcium silicate and the mixture of 50% of tricalcium silicate and 50% of β-dicalcium silicate all expand in solutions of magnesium sulphate (Curves 2A, 2B, 2C, 2S) and that the rate of expansion increases with the concentration of the sulphate solution (Curves 2A and 4A, 2B and 4B).
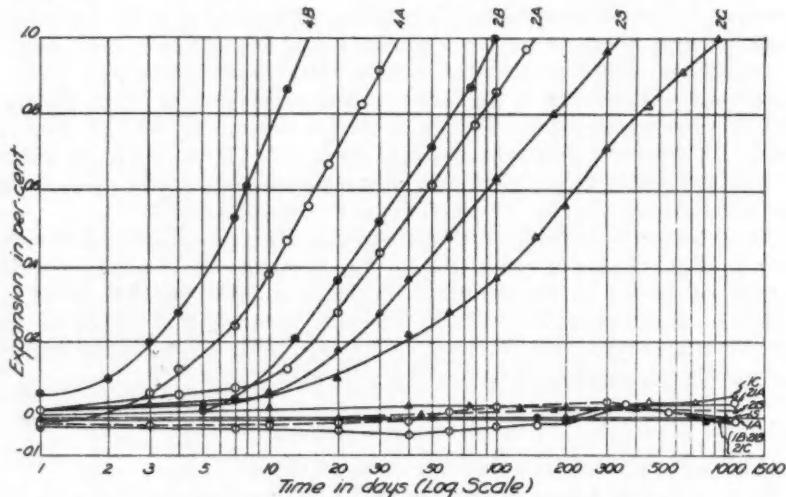
FIG. 1. *Expansion of 1:10 sand mortars made with the calcium silicates as the cement, in 0.15M and 0.50M MgSO₄, 0.15M Na₂SO₄ and a saturated solution of CaSO₄.*
Legend: A = 3CaO.SiO₂; B = β-2CaO.SiO₂; C = γ-2CaO.SiO₂; S = 50% 3CaO.SiO₂ + 50% β-2CaO.SiO₂. 1 = 0.15M Na₂SO₄; 2 = 0.15M MgSO₄; 4 = 0.50M MgSO₄; 21 = Saturated CaSO₄.

In each case the rate of expansion is more rapid for the bars containing β-dicalcium silicate than for bars containing tricalcium silicate cured for the

same length of time (56 days) before exposure (Curves 2A and 2B, 4A and 4B). The very slow expansion of the bars containing γ-dicalcium silicate (Curve 2C) may be in part due to the long curing period of these bars (five months) and in part to the small amount of lime liberated by this compound. It is interesting to note that the bars containing tricalcium silicate and dicalcium silicate in equal proportions (Curves 2S) have a slower rate of expansion than the bars made with either of these silicates alone (Curves 2A and 2B). A comparison of the expansion of the 1:10 silicate mortars with that of similar mortar bars made from Portland cement No. 1 of Table I is shown in Table VI.

TABLE VI

COMPARISON OF TIME REQUIRED FOR LINEAR EXPANSION OF 0.5 AND 1%.
1:10 SAND MORTAR BARS IN $0.15M$ MgSO$_4$ AT 21° C.

Expansion, %	Cement				
	P.C. No. 1	β-2CaO.SiO$_2$	3CaO.SiO$_2$	50% β-2CaO.SiO$_2$ 50% 3CaO.SiO$_2$	γ-2CaO.SiO$_2$
	Serial No.				
	2	2B	2A	2S	2C
	Time in days				
0.5	13	28	35	65	160
1.0	20	100	145	320	900

As the richness of mix is increased, this difference between the rates of expansion of bars made with the pure silicates and of bars made with Portland cement increases rapidly. Thus for 1:5 bars of tricalcium silicate, cured 2 months before exposure to the solution of magnesium sulphate, an expansion of 1% was attained in 1500 days in a 0.16 M solution of magnesium sulphate as against 48 days for similarly treated 1:5 bars of Portland cement No. 1 (Table I). Similar results were obtained when 1:10 and 1:5 bars of β-dicalcium silicate were compared with Portland cement bars of corresponding mix.

Tensile Strength of Silicate Bars Exposed to Magnesium Sulphate

On account of the large amount of material necessary for a systematic determination of loss of tensile or compressive strength during exposure to sulphate solutions, data of this kind are not available. Some of the bars exposed to the solutions were, however, tested for tensile strength in a special clamp which was used in the ordinary briquet testing machine. The determinations were usually made at the time when the expansion measurements were discontinued. The data obtained are shown in Table VII, the tensions being calculated in lb. per sq. in.

Although tension tests of the 1:10 silicate-sand mortars at the time of exposure to the sulphate solutions are not available, other data obtained in this laboratory make it possible to assume that the tensile strength of the tricalcium silicate bars (2A and 4A) would have been considerably below the

TABLE VII

TENSILE STRENGTH OF 1:10 SILICATE BARS AFTER EXPOSURE
TO MAGNESIUM SULPHATE SOLUTIONS

Serial No.	Silicate	Solution	Length of exposure, days	Expansion, %	Tension, lb. per sq. in. after exposure to:	
					Solution	Water
4A	$3CaO.SiO_2$	$0.50M$ $MgSO_4$	210	>2.2	75	
2A	$3CaO.SiO_2$	$0.15M$ $MgSO_4$	200	1.1	65	
2B	β-$2CaO.SiO_2$	$0.15M$ $MgSO_4$	200	1.3	38	
2S	$\{$50% $3CaO.SiO_2$ $\atop$ 50% β-$2CaO.SiO_2$	$0.15M$ $MgSO_4$	325	1.05	42	73 (3 years)
2C	γ-$2CaO.SiO_2$	$0.15M$ $MgSO_4$	1000	1.0	44	10 (3 years)
	Portland cement*	$0.50M$ $MgSO_4$	13	1.0	30	90 (8 weeks)
	Portland cement*	$0.15M$ $MgSO_4$	20	1.0	12	90 (8 weeks)

Cement No. 1, Table I.

value obtained for similar bars of cement No. 1, *i.e.*, 90 lb. per sq. in. The tensile strength of the bars made with β-dicalcium silicate (2B) would have been somewhat more than half of this value at eight weeks. The value for the mixture of the two silicates after three years' exposure to water (2S), 73 lb. per sq. in., may be somewhat low (only one break). It will be seen that the reduction in the tensile strength of the silicate bars after exposure to the sulphate solutions for long periods of time was remarkably small as compared with the rapid loss in strength of similar Portland cement bars. In the case of γ-dicalcium silicate (2C) there is a remarkable increase in strength, probably due to the speeding up of the hydration of this inert silicate by the sulphate.

Similar results were obtained with richer mixes of the silicate, namely, with bars containing one part by weight of the silicate to five parts of standard sand exposed to solutions of magnesium sulphate for longer periods. Bars of tricalcium silicate (1:5) were cured in the damp closet for two months before exposure to a 0.16 M solution of magnesium sulphate. After immersion in the solution for 50 months they had expanded 1.03% of their length and had a tensile strength of 184 lb. per sq. in., as compared with 198 lb. per sq. in. for bars immersed in distilled water. At the end of 80 months' exposure the expansion was only 1.07% and the tension 175 lb. as against 192 lb. per sq. in. obtained for the water blank at that time. In the case of bars of β-dicalcium silicate (1:5) immersed in a 0.16 M solution of magnesium sulphate, a linear expansion of 3.8% was attained in 50 months and the tension was 55 lb. per sq. in. as compared with 187 lb. per sq. in. for similar bars immersed in distilled water. Thus very great expansion takes place before the strength of mortar made of the calcium silicates falls to a low value. In the case of 1:5 bars made with Portland cements immersed in 0.15 M MgSO$_4$, an expansion of 0.25% usually means a loss of 60 to 70%· of the tensile strength while an expansion of 1% usually causes a reduction of about 90% of the original strength.

Expansion Curves for the Silicate Mortars in Solutions of Sodium and
  Calcium Sulphates

The results obtained on exposure of the 1:10 silicate bars to solutions of sodium sulphate and calcium sulphate (Fig. 1.   Curves 1A, 1B, 1C, 1S, 21A, 21B, 21C, 21S, and Table VIII) show a striking contrast to the results of exposures to solutions of magnesium sulphate.   Considering the expansion measurements at the end of three years' exposure there is no evidence of any appreciable deleterious action, the expansion being approximately the same as that obtained on exposure to distilled water.

On exposure of the silicate bars to the solutions there appears to be in general a slight tendency to contract.   This, however, is soon followed by a slight gradual expansion, which usually reaches a maximum after an exposure of about one year, when a second period of very slow contraction of the bars sets in.   The only exceptions to this are the bars of γ-dicalcium silicate in 0.15 M Na_2SO_4 (Curve 1C) which expanded to a maximum of 0.06% elongation at the end of the three-year period and the bars containing tricalcium silicate immersed in saturated calcium sulphate (Curves 21A and 21S) which are still near the maximum expansion of 0.04% and 0.02%, respectively, at the end of three years.   For a summary of the data see Table VIII.

TABLE VIII

EXPANSION OF SILICATE MORTARS (1:10) IN SOLUTIONS OF SODIUM AND CALCIUM SULPHATES

Serial No.	Silicate	Solution	Minimum expansion		Maximum expansion		Expansion after 3 years' exposure, %
			%	Time	%	Time	
3A	3CaO.SiO₂	0.50 M Na_2SO_4	−0.01	10 da.	0.04	1.0 yr.	0.02
1A	3CaO.SiO₂	0.15 M Na_2SO_4	−0.02	{10 da. 3 yr.	0.04	1.0 yr.	−0.02
21A	3CaO.SiO₂	Sat'd CaSO₄	−0.04	50 da.	0.04	1.0 yr.	0.04
3B	β-2CaO.SiO₂	0.50 M Na_2SO_4	−0.01	1 da.	0.05	1.5 yr.	0.03
1B	β-2CaO.SiO₂	0.15 M Na_2SO_4	−0.02	3 yr.	0.00	—	−0.02
21B	β-2CaO.SiO₂	Sat'd CaSO₄	−0.02	3 yr.	0.00	—	−0.02
1C	γ-2CaO.SiO₂	0.15 M Na_2SO_4	0.00	—	0.06	3 yr.	0.06
21C	γ-2CaO.SiO₂	Sat'd CaSO₄	−0.02	50 da.	0.01	1 yr.	−0.01
1S	{50% 3CaO.SiO₂	0.15 M Na_2SO_4	0.00	—	0.02	40 da.	0.02
21S	{50% β-2CaO.SiO₂	Sat'd CaSO₄	0.00	—	0.02	1 yr.	0.02

These results are in agreement with those obtained by Thorvaldson, Vigfusson and Larmour (18) for 1:5 bars of tricalcium silicate and β-dicalcium silicate.   It was thought that leaner mixes might show expansion, but it is now apparent that mortars of the pure silicates are extremely resistant to the action of sodium sulphate and calcium sulphate even where the salt solution has very free access to the particles of hydrated silicate as is certain to be the case with the 1:10 mortar bars.   The possibility of expansion and deterioration taking place after the three-year period of exposure is not excluded and would seem possible or even probable since the solutions have, as indicated later, affected the process of hydrolysis of the silicates in the bars and a microscopic examination of the mortar showed the presence of large quantities of crystals of

gypsum. There is also still the possibility that the strength of the specimens may have been affected without any expansion taking place. No determinations of the tension of the 1:10 mortars after exposure to the solutions of sodium or calcium sulphate have been made. Such data are however available for 1:5 mortar bars of the same cross section (1.55×1.55 cm.) made of tricalcium silicate and β-dicalcium silicate after exposure for four years to solutions of sodium sulphate. The results were as shown in Table IX.

TABLE IX
A COMPARISON OF THE TENSILE STRENGTHS OF BARS OF CEMENT
(CROSS SECTION 1.55×1.55 CM.), AFTER THE EXPOSURES INDICATED

Specification of bar	Tensile strength in lb. per sq. in. after 4 yr. exposure to:		
	Sodium sulphate solutions		Distilled water
	0.6 M	0.16 M	
1:5 Tricalcium silicate	232		198
1:5 β-Dicalcium silicate	256	251	187

Thus the silicate mortar exposed to solutions of sodium sulphate not only showed no appreciable expansion at the end of four years but also had a markedly higher tensile strength than specimens kept the same length of time in distilled water. This observation is not unexpected since specimens of Portland cement mortar exposed to sulphate solutions at first increase in strength more rapidly than similar specimens kept in water (17), and the liberation of lime also proceeds more rapidly and further when Portland cement is exposed to solutions of sodium sulphate than when exposed to pure water (16). As tricalcium aluminate does not liberate lime on hydration, it appears that the sulphate causes a more rapid and greater hydrolysis of the silicates.

These results with the silicate mortars also show a striking contrast to the behavior of similar mortar bars made with a typical Portland cement. Bars of 1:10 mix made with cement No. 1 (Table I) similarly treated and exposed to 0.15 M Na$_2$SO$_4$ showed a linear expansion of 0.04% in eight days and 1% in 15 days. The tension of the bars when exposed to the solution (at eight weeks) was 90 lb. per sq. in. but after 15 days' exposure the tension was less than 5 lb. per sq. in. The corresponding 1:5 mortar bars in 0.50 M Na$_2$SO$_4$ expanded to 0.04% in 14 days and to 1% in 37 days. The initial tension was 270 lb. per sq. in. and the tension at an expansion of 1%, 30 lb. per sq. in. Comparative tests with some 50 commercial Portland cements have shown that the mortar made from this particular cement has a resistance to sulphate solutions well above the average for commercial Portland cements.

II. MORTARS OF THE CALCIUM ALUMINATES AND SAND

Table X shows a summary of the exposures of calcium aluminate mortars (1 part aluminate and 10 parts standard sand by weight) to sulphate solutions. Tricalcium aluminate could not be included in this series of experiments since

the test pieces made of this aluminate and sand soon fall to pieces when exposed to pure water.

TABLE X

EXPOSURE OF 1:10 MORTARS MADE FROM CALCIUM ALUMINATES

Material in bars	Solution				
	MgSO$_4$		Na$_2$SO$_4$		CaSO$_4$
	0.15 M	0.50 M	0.15 M	0.50 M	Saturated at 21° C.
5CaO.3Al$_2$O$_3$	2D	4D	1D	3D	21D
CaO.Al$_2$O$_3$	2E	4E	1E	3E	21E
3CaO.5Al$_2$O$_3$	2F	4F	1F	3F	21F

A similar series of exposures was made with a mortar containing one part of the aluminate to seven and a half parts of standard sand by weight.

The measurement of the expansion of mortar bars of the kind used in this investigation does not appear to be as suitable for the study of the action of sulphates on the pure aluminates as on the silicates. The expansion is often erratic, especially at the beginning of the experiment, this probably being due to the tendency toward localized action of the sulphate and the low stability of the ends made of aluminate paste. This erratic behavior applies more particularly in the case of exposures of these mortars to concentrated solutions of sodium sulphate. The action of sodium sulphate, even in such a lean mortar as 1:10, tends mainly to progress gradually from the surface inwards while the layer of disintegrated material sloughs off as the action advances, leaving an apparently unaffected hard core. The expansion in solutions of magnesium sulphate and calcium sulphate is much

FIG. 2. *Expansion of 1:10 sand mortars made with the calcium aluminates as the cement, in 0.50 M and 0.15 M MgSO$_4$, 0.15 M Na$_2$SO$_4$ and a saturated solution of CaSO$_4$.*
Legend: D = 5 CaO. 3Al$_2$O$_3$; E = CaO. Al$_2$O$_3$; F = 3CaO.5Al$_2$O$_3$; 1 = 0.15 M Na$_2$SO$_4$; 2 = 0.15 M MgSO$_4$; 4 = 0.50 M MgSO$_4$; 21 = Saturated CaSO$_4$.

more regular. Fig. 2 shows the curves for the expansion of the 1:10 bars in 0.15 and 0.50 M solutions of magnesium sulphate, 0.15 M solution of sodium sulphate and in a saturated solution of calcium sulphate. It is evident that the rate of expansion decreases with decreasing percentage of lime in the alumin-

ate, being highest in each case for the bars containing the aluminate
$5CaO.3Al_2O_3$ (Curves D) and lowest for the bars containing $3CaO.5Al_2O_3$
(Curves F).   The rate also increases with the concentration of the sulphate
solution.

While the bars exposed to solutions of sodium sulphate crumbled and shed
their surface layer continuously (in some cases till the cross section of the bar
was about one-quarter of the original), the hard core sometimes expanded 2%
or more before it fell to pieces.   In solutions of magnesium sulphate the bars
did not crumble but kept their shape and remained fairly firm until they had
reached a very high expansion.   In the case of the 1:10 bars of $5CaO.3Al_2O_3$ in
0.50 M $MgSO_4$ (Curve 4D) the maximum expansion was as much as 10% of
the original length, this elongation being attained in the short space of three
days' exposure to the solution.   The corresponding maximum expansion for the
bars of monocalcium aluminate ($CaO.Al_2O_3$) was 5.5% in 7 days (Curve 4E)
and for the $3CaO.5Al_2O_3$ bars 3% in 35 days (Curve 4F).   In the saturated
solution of calcium sulphate the corresponding maximum expansions were
5% in 25 days (Curve 21D), 3.5% in 35 days (Curve 21E) and 2% in 120 days
(Curve 21F).   The expansion and loss in strength for the aluminate mortars
is very rapid compared with that of the mortars made of the calcium silicates.

The aluminate bars of 1:7½ mix were cured in the damp closet for seven days
before they were exposed to the solutions.   The data obtained are shown in
Fig. 3.   The most striking difference between the results of the two series is
the marked increase in resistance which some of the richer mixes exhibit.   The
leaner mix (1:10) contained 9.11% while the richer mix (1:7½) contained
11.76% of the aluminates, an increase of 29%.   In the case of the mortars
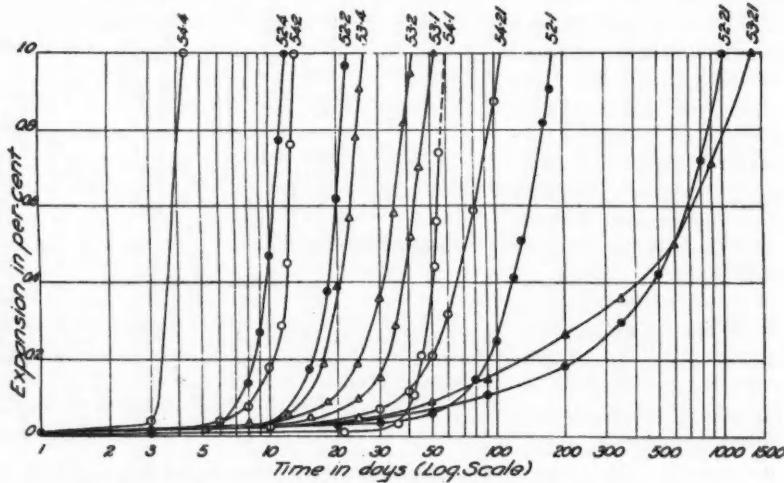
FIG. 3.   *Expansion of 1:7½ sand mortars made with the calcium aluminates as the cement,
in 0.5 M and 0.15 M MgSO₄, 0.15 M Na₂SO₄ and a saturated solution of CaSO₄.*
*Legend: 54 = 5CaO.3Al₂O₃;   52 = CaO.Al₂O₃;   53 = 3CaO.5Al₂O₃.   1 = 0.15M Na₂SO₄;
2 = 0.15M MgSO₄;   4 = 0.50M MgSO₄;   21 = Saturated CaSO₄.*

containing $3CaO.5Al_2O_3$, excepting those immersed in saturated calcium sulphate, there is very little increase in the time required for the $1:7\frac{1}{2}$ bars to reach a given expansion as compared with the 1:10 bars (Fig. 2, Curves 1F, 2F and 4F; Fig. 3, Curves 53-1, 53-2, and 53-4). In the case of the mortars containing monocalcium aluminate the time required for the $1:7\frac{1}{2}$ bars to expand 1% is from 3 times (when exposed to 0.5 M MgSO$_4$, Curves 4E and 52-4) to 50 times (when exposed to saturated CaSO$_4$, Curves 21E and 52-21) as long as the time required for the 1:10 bars. There are also corresponding increases in the time required for an expansion of 1% ranging from 2 to 18 times in the case of the bars containing $5CaO.3Al_2O_3$ (*cf.* Curves 1D and 54-1; 2D and 54-2; 4D and 54-4; 21D and 54-21). It has been found that commercial high alumina cements also show large differences between the resistance of lean and moderately rich mortars to the action of sulphate solutions.

The proportionally greater decrease in the expansion of the $1:7\frac{1}{2}$ bars of monocalcium aluminate causes the rate of expansion in 0.15 M Na$_2$SO$_4$ and in saturated CaSO$_4$ to drop below that of the $1:7\frac{1}{2}$ bars of either $5CaO.3Al_2O_3$ or $3CaO.5Al_2O_3$. The order of the rates of expansion in solutions of magnesium sulphate still remains the same as for the 1:10 bars.

III. THE EFFECT OF THE ADDITION OF THE CALCIUM ALUMINATES, DICALCIUM FERRITE AND THE COMPOUND $4CaO.Al_2O_3,Fe_2O_3$ TO TRICALCIUM SILICATE AND β-DICALCIUM SILICATE

Table XI gives a summary of the composition of the "cement" in the 1:10 sand mortar bars and the solutions in which they were immersed.

TABLE XI

SUMMARY OF EXPOSURES*

Solutions	80% $3CaO.SiO_2$+20% of:					
	C$_3$A	C$_5$A$_3$	CA	C$_3$A$_5$	C$_2$F	C$_4$AF
0.15 M MgSO$_4$	2G	2H	2I	2J	2K	2L
0.15 M Na$_2$SO$_4$	1G	1H	1I	1J	1K	1L
Saturated CaSO$_4$	21G	21H	21I	21J	21K	21L
	80% β-$2CaO.SiO_2$+20% of:					
	C$_3$A	C$_5$A$_3$	CA	C$_3$A$_5$	C$_2$F	C$_4$AF
0.15 M MgSO$_4$	2M	2N	2O	2P	2Q	2R
0.15 M Na$_2$SO$_4$	1M	1N	1O	1P	1Q	1R
Saturated CaSO$_4$	21M	21N	21O	21P	21Q	21R
	40% $3CaO.SiO_2$+40% β-$2CaO.SiO_2$+20% of:					
	C$_3$A	C$_5$A$_3$	CA	C$_3$A$_5$	C$_2$F	C$_4$AF
0.15 M MgSO$_4$	2T	2U	2V	2W	2X	2Y
0.15 M Na$_2$SO$_4$	1T	1U	1V	1W	1X	1Y
Saturated CaSO$_4$	21T	21U	21V	21W	21X	21Y

*C = CaO; S = SiO$_2$; A = Al$_2$O$_3$; F = Fe$_2$O$_3$

1. *Exposures to 0.15 M Solution of Magnesium Sulphate*

Figs. 4 and 5 give the expansion curves for the 1:10 mortars made from the various mixtures outlined in Table XI when exposed to a 0.15 M solution of magnesium sulphate. The expansion curves for the 1:10 silicate mortars are also given for comparison. Substituting 20% of the tricalcium silicate in the mortar with monocalcium aluminate (Curve 2I) or with $3CaO.5Al_2O_3$ (Curve 2J) causes a very rapid increase in the rate of expansion while the presence of 20% of tricalcium aluminate (Curve 2G) or 20% of $5CaO.3Al_2O_3$ (Curve 2H) also gives a very rapidly expanding unstable mortar. The rate of expansion for the first two mortars is actually higher than that for the corresponding mortars
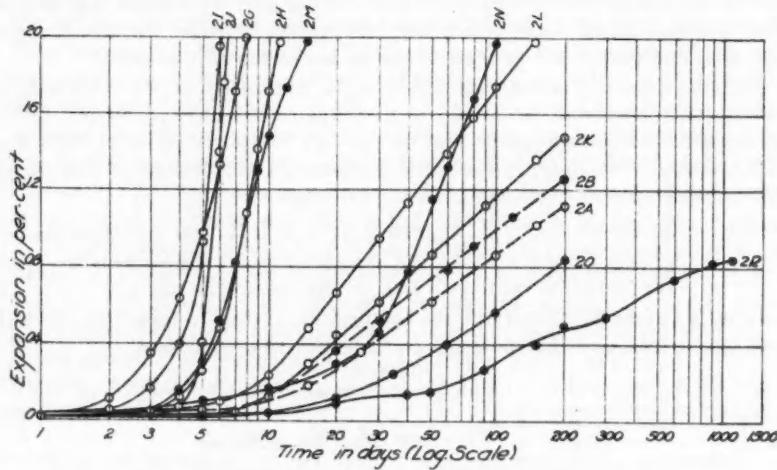
FIG. 4. *Expansion of 1:10 sand mortars made with mixtures of the calcium silicates, calcium aluminates, etc., as the cement, in 0.15 M MgSO₄.*
Legend: $A = 3CaO.SiO_2$; $B = \beta$-$2CaO.SiO_2$; $G = 80\%$ $3CaO.SiO_2$ + 20% $3CaO.Al_2O_3$. $H = 80\%$ $3CaO.SiO_2$ + 20% $5CaO.3Al_2O_3$; $I = 80\%$ $3CaO.SiO_2$ + 20% $CaO.Al_2O_3$. $J = 80\%$ $3CaO.SiO_2$ + 20% $3CaO.5Al_2O_3$; $K = 80\%$ $3CaO.SiO_2$ + 20% $2CaO.Fe_2O_3$. $L = 80\%$ $3CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$. $M = 80\%$ β-$2CaO.SiO_2$ + 20% $3CaO.Al_2O_3$. $N = 80\%$ β-$2CaO.SiO_2$ + 20% $5CaO.3Al_2O_3$; $O = 80\%$ β-$2CaO.SiO_2$ + 20% $CaO.Al_2O_3$. $R = 80\%$ β-$2CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$.

containing the aluminates alone and very much higher than that of the bars made from tricalcium silicate and sand (Curve 2A). The results obtained when the cement is composed of equal parts of tricalcium silicate and β-dicalcium silicate with 20% of the respective aluminates (Fig. 5, Curve 2T, 2U, 2V, 2W) are very similar except that below an expansion of 1% the rate of expansion increases with increasing percentage of lime in the aluminates. When the aluminates are added to β-dicalcium silicate only, the mix containing added tricalcium aluminate (Curve 2M) has a very high rate of expansion and the rate of expansion decreases rapidy with the decreasing percentage of lime in the aluminate present. Substitution of 20% of the β-dicalcium silicate with

$5CaO.3Al_2O_3$ affects the rate of expansion of the mortar only slightly at low expansions, but after reaching an expansion of 0.5% in 35 days the curve is almost as steep as that for tricalcium aluminate. On the other hand, there is a *decrease* in the rate of expansion when one compares a mortar of β-dicalcium silicate with one in which 20% of the β-dicalcium silicate is substituted by monocalcium aluminate, expansions of 0.5% and 0.85% requiring 28 and 70 days respectively, for the former, as against 78 and 300 days respectively, for the latter (Fig. 4, Curves 2B and 2O). A comparison with the cement containing 80% of β-dicalcium silicate and 20% of $3CaO.5Al_2O_3$ was not obtained as
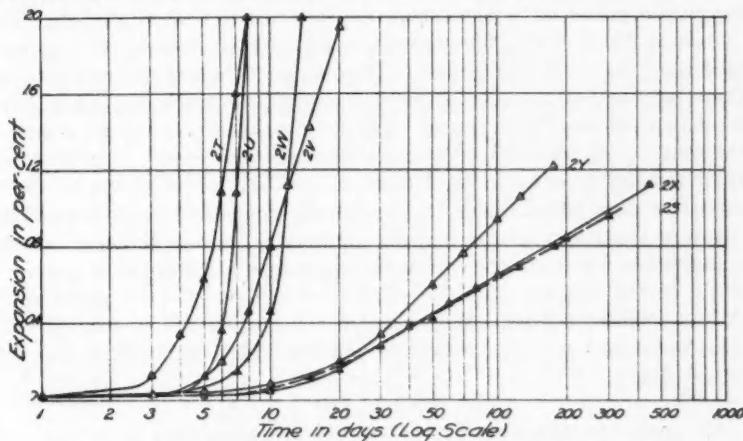

Fig. 5. *Expansion of 1:10 sand mortars made with mixtures of the calcium silicates, aluminates, etc. as the cement, in 0.15 M $MgSO_4$.*
   Legend: $S = 50\%$ $3CaO.SiO_2 + 50\%$ $\beta\text{-}2CaO + SiO_2$;
$T = 40\%$ $3CaO.SiO_2 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $3CaO.Al_2O_3$;
$U = 40\%$ $3CaO.SiO_3 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $5CaO.3Al_2O_3$;
$V = 40\%$ $3CaO.Al_2O_3 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $CaO.Al_2O_3$;
$W = 40\%$ $3CaO.SiO_2 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $3CaO.5Al_2O_3$;
$X = 40\%$ $3CaO.SiO_2 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $2CaO.Fe_2O_3$;
$Y = 40\%$ $3CaO.SiO_2 + 40\%$ $\beta\text{-}2CaO.SiO_2 + 20\%$ $4CaO.Al_2O_3.Fe_2O_3$.

the 1:10 bars were of such low strength when removed from the molds that all broke in handling. Pieces exposed to 0.15 M $MgSO_4$, however, seemed to increase in strength and after an exposure of seven months gave a tension of 87 lb. per sq. in., which is about the same as the tension for 1:10 bars of a high strength Portland cement stored in water.

Substitution of 20% of the tricalcium silicate by dicalcium ferrite or $4CaO.Al_2O_3.Fe_2O_3$ increases the rate of expansion of the mortar materially (Curves 2K and 2L), the effect of $4CaO.Al_2O_3.Fe_2O_3$ being greater than that of dicalcium ferrite. When 20% of the mixture of equal parts of tricalcium silicate and β-dicalcium silicate is substituted by $4CaO.Al_2O_3.Fe_2O_3$ there is only a slight increase in the rate of expansion of the mortar (Fig. 5, Curves 2Y and 2S) while a similar substitution by dicalcium ferrite does not produce an appreciable change. On the other hand, substitution of 20% of the β-dicalcium silicate in a 1:10 mortar by $4CaO.Al_2O_3.Fe_2O_3$ causes a very marked

decrease in the rate of expansion, the time required for a linear expansion of 0.5% being increased from 28 days to 7 months, (Fig. 4, Curves 2B and 2R), and the time for an expansion of 0.85% from 70 days to over 3 years (15 times). A comparison was not obtained with the cement containing 80% of β-dicalcium silicate and 20% of dicalcium ferrite on account of the low strength of the mortar specimens when removed from the molds. Pieces of 1:10 mortar bars exposed to 0.15 M magnesium sulphate seemed, however, to be unaffected after seven months' exposure.

Some fragmentary data are available as to the effect on the tensile strength of the mortar produced by the exposure of the bars to 0.15 M MgSO$_4$. These are given in Table XII. The figures in the column, "expansion", do not in some cases have much significance. The higher values in this column, such as those referring to mixtures containing aluminates, represent the expansion of the bars when they fell to pieces. The lower values represent the expansions at the time the determinations of tensile strength were made. No determinations of tension were made until after an exposure of 200 days so that no quantitative data are available for the rapidly expanding mortars containing mixtures of tricalcium silicate and the aluminates. From the notes made in each case when the measurements were discontinued it is possible to make an estimate of the relative tension. Those marked "very low" probably did not have a tension of above 5 lb. per sq. in., those marked "low" may have had at most twice that strength, and those marked "fairly firm" were slightly in excess of this.

TABLE XII*

EXPANSION AND TENSILE STRENGTH OF 1:10 MORTARS EXPOSED TO 0.15 M MgSO$_4$

Serial No.	Cement	Expansion, %	Time of exposure, days	Tensile strength, lb. per sq. in.
2A	C_3S	1.12	200	65
2B	β-C_2S	1.26	200	38
2S	50% C_3S+50% β-C_2S	1.05	325	42
2G	80% C_3S+20% C_3A	4.86	26	Low
2H	80% C_3S+20% C_5A_3	4.69	26	Low
2I	80% C_3S+20% CA	6.27	10	Very low
2J	80% C_3S+20% C_3A_5	5.50	10	Very low
2K	80% C_3S+20% C_2F	1.48	200	48
2L	80% C_3S+20% C_4AF	2.04	160	Bars firm
2T	40% C_3S+40% β-C_2S+20% C_3A	3.08	11	Low
2U	40% C_3S+40% β-C_2S+20% C_5A_3	3.58	10	Very low
2V	40% C_3S+40% β-C_2S+20% CA	3.00	45	Bars fairly firm
2W	40% C_3S+40% β-C_2S+20% C_3A_5	3.32	16	Low
2X	40% C_3S+40% β-C_2S+20% C_2F	1.11	450	86
2Y	40% C_3S+40% β-C_2S+20% C_4AF	>1.22	200	60
2M	80% β-C_2S+20% C_3A	3.05	35	Bars fairly firm
2N	80% β-C_2S+20% C_5A_3	>2.10	210	60
2O	80% β-C_2S+20% CA	>0.85	300	81
2P	80% β-C_2S+20% C_3A_5		200	87
2Q	80% β-C_2S+20% C_2F	—		No test
2R	80% β-C_2S+20% C_4AF	0.85	1100	No test

*$C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3$.

It will be seen from Table XII that all the mortars which expanded rapidly also lost their strength rapidly, while those which expanded slowly retained considerable strength even after long exposures to the sulphate solution. Further, the substitution of 20% of the mixed silicates by either dicalcium ferrite or $4CaO.Al_2O_3.Fe_2O_3$ or the substitution of 20% of β-dicalcium silicate by either monocalcium aluminate or $3CaO.5Al_2O_3$ gave mortars which retained their strength better than those made with the corresponding silicates alone, and in some cases after an exposure of from 6 to 15 months gave a tension nearly equal to that of Portland cement of the same mix stored in fresh water.

2. *Exposures to Saturated CaSO₄ and to 0.15 M Na₂SO₄*

Figs. 6 and 7 give the expansion data for this series of experiments. When 1:10 mortars made from cements containing 80% of the calcium silicates with
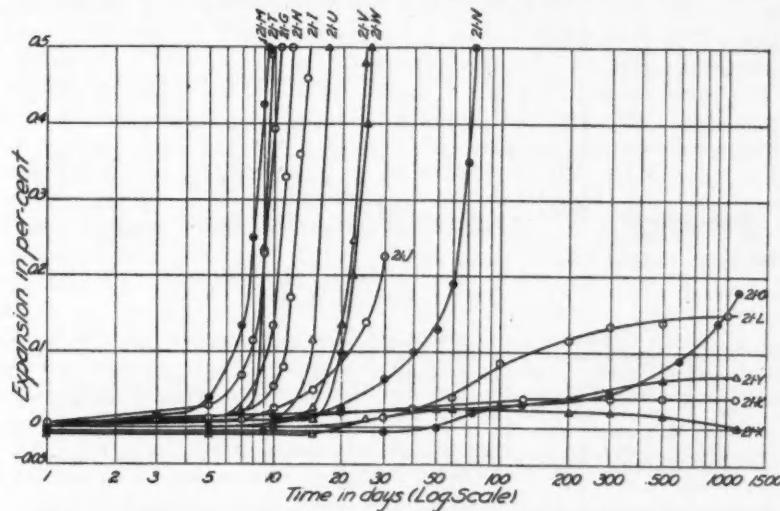
FIG. 6 *Expansion of 1:10 sand mortars made with mixtures of the calcium silicates, aluminates, etc. as the cement, in a saturated solution of CaSO₄.*
   Legend: G, H, I, J, K, and L = 80% 3CaO.SiO₂ with 20% of 3CaO.Al₂O₃, 5CaO.3Al₂O₃, CaO.Al₂O₃, 3CaO.5Al₂O₃, 2CaO.Fe₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, respectively. M, N, and O = 80% β-2CaO.SiO₂ with 20% of 3CaO.Al₂O₃, 5CaO.3Al₂O₃ and CaO.Al₂O₃, respectively. T, U, V, W, X and Y = 40% 3CaO.SiO₂+40% β-2CaO.SiO₂ with 20% of 3CaO.Al₂O₃, 5CaO.3Al₂O₃, CaO.Al₂O₃, 3CaO.5Al₂O₃, 2CaO.Fe₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, respectively.

20% of the various calcium aluminates were exposed to a saturated solution of calcium sulphate the rate of expansion was in general low for the first few days followed by a period of more rapid expansion. Considering each of the three basic silicate cements, (1) 100% C₃S, (2) 50% C₃S + 50% β-C₂S, (3)100% β-C₂S, in turn, one finds that the length of the period of slow expansion was increased as the proportion of lime in the substituting aluminate decreased, *i.e.*, in the order $3CaO.Al_2O_3 < 5CaO.3Al_2O_3 < CaO.Al_2O_3 < 3CaO.5Al_2O_3$. (Curves G, H, I, and J; T, U, V, and W; M, N, and O). In the case of the

mortars highest in tricalcium silicate there was a marked amount of crumbling and an early decrease in strength when exposed to 0.15 M Na$_2$SO$_4$ as shown by the fact that the expansion curves come to an end at very low expansions (Curves 1G, 1H, 1I and 1J).   The mortar containing 80% of tricalcium silicate and 20% of monocalcium aluminate actually crumbled to pieces after an exposure of six days after a linear expansion of slightly over 0.03% (1I).
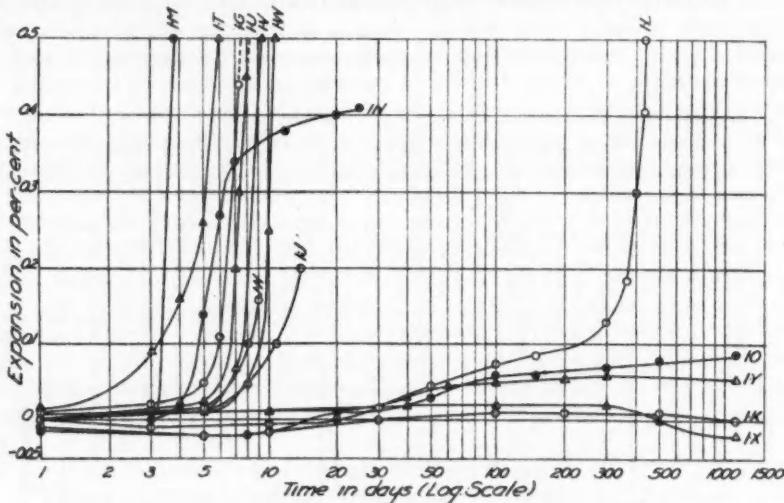
FIG. 7. *Expansion of 1:10 sand mortars made with mixtures of the calcium silicates, aluminates, etc. as the cement, in a 0.15 M Na$_2$SO$_4$.*
Legend: G, H, J, K and L=80% 3CaO.SiO$_2$ with 20% of 3CaO.Al$_2$O$_3$, 5CaO.3Al$_2$O$_3$, 3CaO.5Al$_2$O$_3$, 2CaO.Fe$_2$O$_3$ and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, respectively. M, N and O=80% β-2CaO.SiO$_2$ with 20% 3CaO.Al$_2$O$_3$, 5CaO.3Al$_2$O$_3$ and CaO.Al$_2$O$_3$, respectively. T, U, V, W, X and Y=40% 3CaO.SiO$_2$+40% β-2CaO.SiO$_2$ with 20% of 3CaO.Al$_2$O$_3$, 5CaO.3Al$_2$O$_3$, CaO.Al$_2$O$_3$, 3CaO.5Al$_2$O$_3$, 2CaO.Fe$_2$O$_3$ and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, respectively.

It is rather remarkable that while 1:10 sand mortars made with tricalcium silicate and similar mortars made with tricalcium silicate and β-dicalcium silicate in equal proportions were apparently not affected by exposures to a saturated solution of calcium sulphate or a 0.15 M solution of sodium sulphate for a period of three years, the corresponding mortars in which only 20% of the silicate was substituted by the various calcium aluminates expanded in these solutions as a rule faster than similar mortars made from the corresponding calcium aluminate.   The same applies to mortars made with a cement containing 80% of the mixed silicates, the balance being composed of the mixed aluminates.

The substitution of 20% of the tricalcium silicate by dicalcium ferrite and a similar substitution in the case of the cement containing equal proportions of tricalcium silicate and β-dicalcium silicate gave mortars which showed almost no change in expansion as compared with the corresponding silicate mortars at the end of three years exposure (Curves 1K, 1X, 21K, 21X).   Similar substitutions

by the compound $4CaO.Al_2O_3.Fe_2O_3$ increased the rate of expansion of the tricalcium silicate mortar materially, giving a linear expansion of 0.7% in 16 months when exposed to $0.15\ M$ Na_2SO_4 (Curve 1L) and an expansion of 0.16% in three years in the saturated solution of calcium sulphate (Curve 21L). On the other hand, in the case of the mortar containing tricalcium silicate and β-dicalcium silicate in equal proportions, the substitution by $4CaO.Al_2O_3.Fe_2O_3$ increased the expansion only very slightly as compared with the mortar made from the pure silicates (namely, 0.05% in $0.15\ M$ Na_2SO_4, Curve 1Y, and 0.09% in saturated $CaSO_4$, Curve 21Y, at the end of three years as compared with 0.00% and 0.02% for the pure silicate mortar in the respective solutions, Curves 1S and 21S).

The 1:10 mortar bars made from the cement containing 80% of β-dicalcium silicate with 20% of the various aluminates gave rates of expansion which were in the same order as those for the corresponding tricalcium silicate plus aluminate mortars. The rate of expansion for the bars containing tricalcium aluminate was very rapid in both solutions (Curves 1M and 21M). The expansion of the mortar containing 20% of $5CaO.3Al_2O_3$ (Curves 1N and 21N) was very much slower, and the bars were fairly resistant to the action of the solutions, as shown by the fact that the tension of the bars after exposure for seven months was 67 lb. per sq. in. for those in $0.15\ M$ Na_2SO_4 and 71 lb. per sq. in. for those in saturated $CaSO_4$. The mortar made from the cement of the composition 80% β-$2CaO.SiO_2$ $+$ 20% $CaO.Al_2O_3$ was extremely resistant to both solutions. When exposed to saturated $CaSO_4$ it reached a linear expansion of 0.1% in 24 months (Curve 21O), while in $0.15\ M$ Na_2SO_4 it had not reached this expansion after three years' exposure (Curve 1O). Bars containing 80% β-$2CaO.SiO_2$ $+$ 20% $3CaO.5Al_2O_3$ were not measured but appeared to be in good condition after seven months' exposure and had then a tension of 43 lb. per sq. in. for those in $0.15\ M$ Na_2SO_4 and 60 lb. for those in the saturated solution of $CaSO_4$.

No measurements of expansion of the bars containing dicalcium ferrite or $4CaO.Al_2O_3.Fe_2O_3$ added to β-dicalcium silicate were obtained. Examination of pieces of bars exposed to the solutions indicated, however, that they were highly resistant to the action of the solutions. The bars made with 80% of β-dicalcium silicate and 20% of $4CaO.Al_2O_3.Fe_2O_3$ had a tension of 48 lb. per sq. in. after seven months' exposure to $0.15\ M$ Na_2SO_4. In considering the tension data one must bear in mind that the addition of dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$ to the silicates gave bars which had very low strengths when placed in the solutions. The tensions obtained after the above exposures of these bars were probably in all cases higher than at the time of immersion in the solutions.

Discussion of the Results Obtained with Mortars of Mixed Silicates and Aluminates

The most interesting observation made is the striking difference between the behavior on exposure to sulphate solutions of mortars made from mixtures of the aluminates with tricalcium silicate as the basic material on the one hand

and with β-dicalcium silicate as the basic material on the other   The expansion obtained with mortars made of such mixtures cannot be calculated from the behavior of the corresponding mortars made from the pure substances and exposed to the same solutions under similar conditions.   The curves already given show that when the cementing material contained 80% of tricalcium silicate, the balance being in turn tricalcium aluminate, $5CaO.3Al_2O_3$, monocalcium aluminate and $3CaO.5Al_2O_3$, the resulting mortars were extremely unstable in sulphate solutions, exhibiting very rapid volume changes and loss of strength out of proportion to what would have been expected from the behavior of similar mortars made from the individual substances.   This was also the case when the tricalcium silicate was substituted by a mixture of tricalcium silicate and β-dicalcium silicate in equal proportions, with the aluminate remaining the same.   In general it may be said that the presence of any of the calcium aluminates in a cement containing a large quantity of tricalcium silicate renders mortars made from it very unstable in sulphate solutions.   It should be noted here that aluminates low in lime are not likely to be present in the product of a mix high in lime calcined until equilibrium is attained.   Incomplete burning or the firing of a kiln at a temperature above the decomposition point of tricalcium aluminate might cause the presence of $5CaO.3Al_2O_3$ in the calcined product.

The picture is changed very materially when one considers the presence of the aluminates in a cement of which β-dicalcium silicate is the base.   The mortar containing a considerable quantity of tricalcium aluminate was still quite unstable in all the sulphate solutions.   The mortar made with a cement containing 80% β-$2CaO.SiO_2$ + 20% $5CaO.3Al_2O_3$ showed marked signs of increased stability.   The expansion was slowed down, although still high, and the mortar retained its strength remarkably well.   Tension tests on the 1:10 mortars gave after seven months' exposure 60 lb. per sq. in. in 0.15 M $MgSO_4$, 67 lb. per sq. in. in 0.15 M Na_2SO_4 and 71 lb. per sq. in. in saturated $CaSO_4$. Admixture of monocalcium aluminate, which in the presence of large amounts of tricalcium silicate gave perhaps the most unstable mortar, gave a remarkable result when β-dicalcium silicate was the basic material.   The 1:10 mortar made with the cement containing 80% of β-dicalcium silicate and 20% of monocalcium aluminate had a much higher stability in 0.15 M $MgSO_4$ than the corresponding mortar made with the pure silicate.   At the end of seven months' exposure, it gave an expansion of 0.85% and after 10 months' exposure, a tension of 80 lb. per sq. in. as against an expansion of 1.26% and a tension of 38 lb. per sq. in. for the pure silicate mortar at the end of seven months' exposure. The expansion of this mortar in 0.15 M Na_2SO_4 and saturated $CaSO_4$ was very low indeed (0.09% and 0.18% respectively at the end of three years' exposure) although somewhat greater than that of the pure silicate mortar in the same solutions.

The anomalous behavior of mixtures containing tricalcium silicate and β-dicalcium silicate respectively was also evident when $4CaO.Al_2O_3.Fe_2O_3$ was present in the cement mixture.   Sand mortar (1:10) made with a cement composed of 80% of tricalcium silicate and 20% of $4CaO.Al_2O_3.Fe_2O_3$ expanded

in all three sulphate solutions much faster than the corresponding mortar made with a cement of pure tricalcium silicate. This was especially marked in 0.15 M MgSO$_4$ and after long exposure to 0.15 M Na$_2$SO$_4$. On the other hand, when β-dicalcium silicate was substituted for the tricalcium silicate, the amount of 4CaO.Al$_2$O$_3$,Fe$_2$O$_3$ remaining the same, the mortar expanded much more slowly in 0.15 M MgSO$_4$ than the corresponding sand mortar made with pure β-dicalcium silicate (0.84% in three years as compared with 0.84% in 70 days). The expansion curves for this mortar in 0.15 M Na$_2$SO$_4$ and saturated CaSO$_4$ are not available.

It is evident that the compound 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ is not as sensitive to the adverse effect of the presence of tricalcium silicate in the mortar as are the calcium aluminates. When 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ was present to the extent of 20% in the cement containing tricalcium silicate and β-dicalcium silicate in equal proportions, the speeding up of the expansion, as compared with that of the pure silicate cement, was marked only in the 0.15 M MgSO$_4$. The expansions at the end of three years' exposure to 0.15 M Na$_2$SO$_4$ and saturated CaSO$_4$ were 0.05% and 0.07%, respectively, which were only slighty in excess of the maximum expansion of the mortar made with the silicate. The figures in Table XIII illustrate the effect of the silicate on the expansion in 0.15 M MgSO$_4$ of mortars containing 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$.

When dicalcium ferrite was substituted for the 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ in the above mortars there was an increase in the rate of expansion as compared with that of the corresponding silicate mortar only in the case of the mortar made from the cement containing 80% of tricalcium silicate and only for exposure to 0.15 M MgSO$_4$. The expansion curve for the mortar containing the silicate mixture with the dicalcium ferrite was practically the same as for the corresponding silicate mortar. The substitution of 20% of the silicates by dicalcium ferrite had no appreciable effect on the expansion in 0.15 M Na$_2$SO$_4$ or saturated CaSO$_4$.

TABLE XIII

EFFECT OF TRICALCIUM SILICATE ON THE EXPANSION OF MORTARS CONTAINING
4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, AND IMMERSED IN 0.15 M MgSO$_4$

Cement in 1:10 sand mortar	C$_3$S	80% C$_3$S 20% C$_4$AF	50% C$_3$S 50% β-C$_2$S	40% C$_3$S 40% β-C$_2$S 20% C$_4$AF	β-C$_2$S	80% β-C$_2$S 20% C$_4$AF
Time in days necessary for expansion of 0.84%	98	56	195	85	70	1095 (3 yr.)

The adverse effect produced by a high content of tricalcium silicate is thus most evident when the mortar is exposed to a solution of magnesium sulphate. The effect is, however, probably just as great in solutions of sodium and calcium sulphate but becomes noticeable earlier in solutions of magnesium sulphate on account of the aggressive action of this salt on the silicates. In each of the solutions the effect is greatest with cements containing the calcium aluminates,

much smaller when the compound $4CaO.Al_2O_3.Fe_2O_3$ is present, and where dicalcium ferrite is present, is apparent only in the cement containing 80% of tricalcium silicate exposed to 0.15 M $MgSO_4$. On the other hand, the beneficial effect on the resistance to sulphates observed when β-dicalcium silicate is the basic substance, is apparent in 0.15 M $MgSO_4$ when 20% of monocalcium aluminate is present, appears to be more marked with the aluminate, $3CaO.5Al_2O_3$, and is very pronounced with the compound $4CaO.Al_2O_3.Fe_2O_3$.

Application to Commercial Portland Cement

Fig. 8 gives the expansion curves for the synthetic cements which showed, in the form of a 1:10 sand mortar, a very materially increased resistance to the action of sulphates as compared with commercial Portland cements. Since
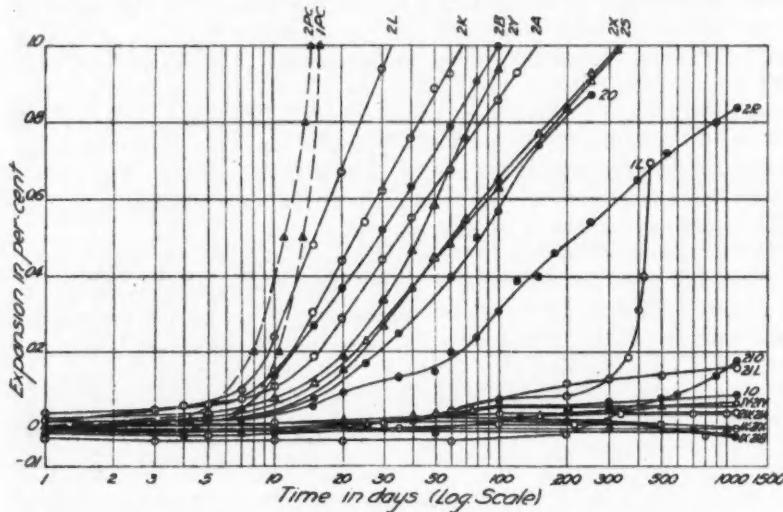
FIG. 8. Expansion in sulphate solutions of 1:10 sand mortars made with mixtures of calcium silicates, aluminates, etc. which are more resistant to the solutions than the average commercial Portland cement.
Legend: P.C. = Portland cement (average of eight cements). A = 3CaO.SiO₂; B = β-2CaO.SiO₂; K and L = 80% 3CaO.SiO₂ with 20% of 2CaO.Fe₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, respectively; O and R = 80% β-2CaO.SiO₂ with 20% of CaO.Al₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, respectively. S = 50% 3CaO.SiO₂+50% β-2CaO.SiO₂. X and Y = 40% 3CaO.SiO₂+ 40% β-2CaO.SiO₂ with 20% of 2CaO.Fe₂O₃ and 4CaO.Al₂O₃.Fe₂O₃, respectively. 1 = 0.15 M Na₂SO₄; 2 = 0.15 M MgSO₄; 21 = Saturated CaSO₄.

their resistance was lower or only slightly in excess of that of Portland cement, the following synthetic cements are omitted: All those containing 20% of the calcium aluminates with 80% of tricalcium silicate or with the mixture of 40% of tricalcium silicate and 40% of β-dicalcium silicate, and those containing either 20% of tricalcium aluminate or 20% of $5CaO.3Al_2O_3$ with 80% of β-dicalcium silicate. The resistance of the last named is, however, higher than that of Portland cement. A few of the synthetic cements which gave evidence of great resistance to sulphate solutions but which gave such a weak 1:10 sand

mortar that all the bars were damaged when they were removed from the molds also had to be omitted. These include the mixture of 80% of β-dicalcium silicate and 20% of $3CaO.5Al_2O_3$, 80% of β-dicalcium silicate and 20% of dicalcium ferrite. There is, for the same reason, only a partial set of data for the mixture containing 80% of β-dicalcium silicate and 20% of $4CaO.Al_2O_3.Fe_2O_3$. A few curves very close to the horizontal axis are omitted owing to crowding. These include curves for the mortar made with tricalcium silicate and exposed to 0.15 M Na_2SO_4, the β-dicalcium silicate mortar exposed to 0.15 M Na_2SO_4 and the mortar made with the mixture of the two silicates and exposed to 0.15 M Na_2SO_4 and saturated $CaSO_4$. Included also are curves for 1:10 Portland cement mortar exposed to 0.15 M Na_2SO_4 (Curve 1 PC) and 0.15 M $MgSO_4$ (Curve 2 PC). These represent the average of the data obtained with eight commercial Portland cements manufactured in eight different cement plants in Canada and the United States.

The gypsum present in commercial Portland cements is of importance in regulating the set of the cement. This action appears to be due at least in part to modification of the solubility and hydration of the calcium aluminate in the cement (5). Test pieces made with a ground Portland cement clinker without the addition of gypsum generally give lower strengths than similar test pieces made with the same cement after addition of gypsum. No gypsum was added to any of the experimental cements described in this paper. It may be concluded, therefore, that in the case of at least some of the composite mixes, especially those containing mixtures of the silicates and calcium aluminates, the strength of the test pieces was lower than would have been the case if gypsum had been added. The effect of this on the comparative results obtained is, however, probably very slight, as the strength of the test pieces— once they are strong enough to be handled without breakage—is of minor importance under the conditions of the experiments. When concrete test pieces are exposed to sulphate solutions under conditions of alternate freezing and thawing, or where the test pieces are partly exposed to the air, the porosity and strength are of very great importance in determining the permanency. When, however, the test pieces are completely immersed in the sulphate solution at constant temperature the strength plays only a very secondary role. Many examples showing this are available. The 1:10 mortar made with γ-dicalcium silicate, which had a tensile strength of only 10 lb. per sq. in. after three years' curing in water, stood up extremely well in the three sulphate solutions, giving a slower rate of expansion in solutions of calcium and magnesium sulphate than similar mortar made with tricalcium silicate, although the latter had many times the strength of the former. The mortar bars made with cement I (80% $3CaO.SiO_2$ + 20% $CaO.Al_2O_3$) which had a tensile strength of 60 lb. per sq. in. when exposed to 0.15 M $MgSO_4$ expanded 1% in five days, while those made with cement K (80% $3CaO.SiO_2$ + 20% $2CaO.Fe_2O_3$) which had a tensile strength of 47 lb. per sq. in. when exposed, required 70 days to expand the same amount. The bars made with cement R (80% β-$2CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$), having a tensile strength of 20 lb. per sq. in., expanded only 0.84% after an exposure to the same solution for three years. It thus

appears that the differences in the chemical reactions have the predominating influence and the strength of the specimens only a minor one. Experiments with a large number of commercial Portland cements have shown also that the strength developed by the cement has only a very slight influence on the rate of expansion or the loss of strength of its test pieces, when exposed to sulphate solutions under conditions of complete immersion at a constant temperature. It may be assumed, therefore, that while the presence of gypsum would have modified somewhat the strength of the mortars made from the composite cements, nevertheless the effect on the expansion would have been slight, and that in general the information obtained as to the resistance of the various compounds to sulphate solutions is applicable to commercial cements.

In considering the significance of the actual time required for any particular linear expansion of the experimental mortars it must be remembered that the very lean mortar and the conditions of treatment and exposure render the tests extremely severe. A comparison of the expansion curves for the experimental mortars with those for similar mortars made of commercial Portland cements makes it possible to obtain a quantitative measure or ratio of the relative resistance of any of the composite cements and Portland cement. Since this comparison is based only on the linear expansion of the mortars and since it was found that the tensile strength of these fell off much more slowly with increasing length than that of similar mortars made with Portland cement, it is evident that the ratio obtained gives a minimum value for increased resistance.

TABLE XIV

EXPANSION OF MORTAR BARS IN 0.15 M Na_2SO_4

Cement	Ratio, Cement : sand			
	1:10	1:5	1:3	1:2
	Time in days for expansion of 0.50%			
A	9.2	12.3	31.8	125
B	10.0	19.2	89	450
Ratio B/A	1.09	1.56	2.80	3.60

When considering the relation between the life of a specimen of a 1:10 sand mortar exposed to sulphate action and that of concrete or rich mix there are two facts which must be remembered: First, when the proportion of cement in a mortar is increased, the resistance of the mortar increases up to a certain limit; second, a slight difference in the relative resistance of two cements, as shown by expansion measurements of very lean mortars, may be greatly magnified when the richness of mix is increased. This is illustrated by the data obtained with two commercial Portland cements A and B, as given in Table XIV (19).

Assuming the resistance to be directly proportional to the time required for an expansion of 0.50%, one finds that as the mix changes from 1:10 to 1:2 the

resistance of the less resistant cement, A, increases 13 times while the increase for the more resistant cement, B, is 45 times. Considering the 1:10 mortar, it appears that Cement B is 9% more resistant than Cement A while from the results with the 1:2 mortar Cement B appears to be 360% more resistant than Cement A. When one exposes the mortar to 0.15 M MgSO$_4$ instead of to Na$_2$SO$_4$ the decrease in the rate of expansion with increasing richness of mix is even more marked.

Table XV gives the time required for an expansion of 0.50% for the mortars made from the experimental cements (Fig. 8) which showed a higher resistance than the average of the eight commercial Portland cements when exposed to 0.15 M MgSO$_4$. It also gives the ratio for each of the mortars on the basis of unity for the average Portland cement. The cements are also arranged in order of increasing resistance to 0.15 M MgSO$_4$. It will be seen that the time for an expansion of 0.5% increases from 140% in the case of Cement L (80% 3CaO.SiO$_2$ + 20% 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$) to 1910% in the case of Cement R (80% β-2CaO.SiO$_2$ + 20% 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$) as compared with 100% for the average of the eight commercial Portland cements.

The available data on the tensile strength of the mortar bars after exposures for various time intervals to 0.15 M MgSO$_4$ are also given in Table XV. Although these were not made systematically at a definite linear expansion, they give valuable information when considered with reference both to the corresponding linear expansion and length of exposure to the solution. The retention of strength by the mortars made from the synthetic cements, after long periods of exposure and at high expansion, is very striking when compared with the average for the Portland cements.

TABLE XV

DATA ON EXPANSION AND TENSILE STRENGTH OF 1:10 MORTARS IN 0.15 M MgSO$_4$

Data	Cements									
	P.C.	L	K	B	A	Y	X	S	O	R
Time in days for expansion of 0.50%	11	15.5	23.0	29	35	43	60	65	85	210
Ratio (time for P.C. = 1)	1.0	1.4	2.1	2.6	3.2	3.9	5.5	5.9	7.7	19.1
Expansion when broken, %	1.0	2.04	1.48	1.26	>1.12	1.22	1.11	1.05	0.85	0.85
Time of exposure in days	15	160	200	200	200	200	450	325	300	1100
Tensile strength, lb. per sq. in.	10	*	48	38	65	60	86	42	81	†
Blank, 3 yr. in water, tensile strength lb. per sq. in.		>45	>47	–	–	102	92	73	–	–

*Not determined, bars firm.
†Not determined, bars still being measured.

Reference to Figs. 4, 5, 6, and 7 shows that for the synthetic cements of low resistance to sulphates the rate of expansion of the 1:10 mortars in 0.15 M MgSO$_4$ does not differ much from that in 0.15 M Na$_2$SO$_4$. The same applies to 1:10 mortars made with Portland cement (Fig. 8, Curves 2 P.C. and 1 P.C.).

On the other hand it is evident (Fig. 8) that the more resistant cements have developed an extremely high resistance to the action of solutions of sodium sulphate and calcium sulphate as compared with their resistance to 0.15 M $MgSO_4$. In only one case (1L, 80% $3CaO.SiO_2$ + 20% $4CaO.Al_2O_3$ Fe_2O_3 in 0.15 M Na_2SO_4) has one of the experimental mortars of Fig. 8 reached an expansion of 0.50% by the end of the three-year period of exposure, the time required being 32 times that of the average for the Portland cements. The mortar having the next greatest expansion (21O, 80% β-$2CaO.SiO_2$ + 20% $CaO.Al_2O_3$ in saturated $CaSO_4$) has required 110 times as long as the Portland cements for a linear expansion of 0.09%.

In view of the change in the resistance of Portland cement mortars when the richness of mix is increased, and the results obtained with 1:5 sand mortars of the pure silicates, one might interpret the data of Fig. 8 and Table XV, with reference to concretes of rich mix made with these cements, as follows:

Cements L and K would show very much increased resistance to the action of sulphate solutions as compared with concrete made from the usual commercial Portland cements. Cement L (80% $3CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$) would, however, be subject to failure in water containing magnesium sulphate and probably after very long exposure to water containing sodium sulphate while some deterioration might take place in saturated calcium sulphate. Cement K (80% $3CaO.SiO_2$ + 20% $2CaO.Fe_2O_3$) while more resistant to solutions of magnesium sulphate would yet be subject to failure, but would give a concrete which is practically permanent in solutions of sodium and calcium sulphates.

Cements X and Y, while subject to the action of magnesium sulphate, would, in the form of rich concrete, have a life many times that of ordinary Portland cement, and under moderately severe conditions of exposure would probably approach permanency, especially in the case of rich concrete made with Cement X (40% $3CaO.SiO_2$ + 40% β-$2CaO.SiO_2$ + 20% $2CaO.Fe_2O_3$). Cement Y (40% $3CaO.SiO_2$ + 40% β-$2CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$) would be somewhat more vulnerable. Both cements would give a concrete which would be practically permanent under exposure to water containing sodium or calcium sulphate.

Cement O (80% β-$2CaO.SiO_2$ + 20% $CaO.Al_2O_3$) would be slightly more resistant to solutions of magnesium sulphate than Cement X. It would, however, be less resistant than either X or Y to the action of calcium sulphate.

Cement R (80% β-$2CaO.SiO_2$ + 20% $4CaO.Al_2O_3.Fe_2O_3$) although slightly attacked in the form of a lean mortar by solutions of magnesium sulphate would have such a long life as to be practically immune in the form of a rich concrete. The early strength would, however, be very low.

It is now generally accepted that the compounds present is a well-burned Portland cement clinker are tricalcium silicate ($3CaO.SiO_2$), β-dicalcium silicate (β-$2CaO.SiO_2$), the compound $4CaO.Al_2O_3.Fe_2O_3$ and tricalcium aluminate ($3CaO.Al_2O_3$) while the magnesium oxide is probably present in the free state (6, 7, 11, 12). The fluxing materials are the iron compound and the tricalcium aluminate. The presence of magnesium oxide also lowers the

temperature of clinker formation (6).   If there is more than sufficient iron oxide present to combine with all the alumina to form $4CaO.Al_2O_3.Fe_2O_3$, the excess of iron forms dicalcium ferrite ($2CaO.Fe_2O_3$).   This is the case in iron-ore cement which was developed by Michaelis.   The modern tendency in the manufacture of Portland cement is to increase the percentage of lime in the raw mix so as to increase the proportion of tricalcium silicate in the product and thus obtain high early strength.   The same applies to iron-ore cements which tend to have a very low early strength unless high in tricalcium silicate and finely ground.

It is evident from Fig. 8 and Table XV that one cannot expect to obtain a cement of the Portland cement type high in tricalcium silicate which is at the same time very highly resistant to solutions of either magnesium or sodium sulphate.   If the necessary fluxing material in the raw mix is alumina, with little iron present, the resulting cement high in tricalcium silicate will be extremely unstable in all three sulphate solutions.   If the amount of alumina is reduced and more iron is present, to give fluxing material favoring combination of the silica and lime, the resistance to all the sulphate solutions is increased, but the limiting value obtained when there is enough iron present to combine with all the alumina, falls far short of the resistance of the basic tricalcium silicate.   If the alumina is eliminated from the raw mix and the fluxing material is dicalcium ferrite, the resulting iron-ore cement still falls short of the resistance of pure tricalcium silicate when exposed to solutions of magnesium sulphate, but is very resistant to the action of solutions of sodium and calcium sulphate.

It is thus clearly indicated that the first requirement in order to produce a highly resistant cement is to reduce the amount of tricalcium silicate it contains. If this is reduced so that there are equal proportions of the two basic silicates and the fluxing material is alumina the cement will still be extremely unstable in sulphate solutions.   If the alumina is now reduced in amount and the iron is increased until all the alumina has combined with the ferric oxide, a cement which is probably more resistant to magnesium sulphate than pure tricalcium silicate is produced (Curves 2Y and 2A).   The expansion is, however, greater than for the cement of the mixed silicates (2S).   The effect of solutions of sodium and calcium sulphate on this cement is quite small (Curves 1Y and 21Y).   The corresponding iron-ore cement produced by eliminating the alumina from the mix and substituting ferric oxide as flux gives a cement which is as stable in $0.15M$ $MgSO_4$ as the basic silicate mixture (Curves 2X and 2S) and practically immune to the action of sodium and calcium sulphate (Curves 1X and 21X).

In order to obtain a cement which is more highly resistant to magnesium sulphate than the basic silicates, it is necessary to reduce the proportion of tricalcium silicate to less than one-half of the amount of silicates present in the cement.   How far the resistance can be safely increased in this way depends on the requirements of early strength.   Apart from requirements of strength one would expect that the most resistant material would be obtained in the case of Portland cement when enough iron oxide is present to combine with

all the alumina (Curve 2R) and in the case of iron-ore cement, when all the alumina is displaced by iron oxide, all the silica, in both cases, being present as dicalcium silicate.

It has already been shown that a mortar made from a cement containing tricalcium silicate with any of the calcium aluminates present is very unstable in sulphate solutions. It follows that high alumina cements should contain no tricalcium silicate and that the silica should be present in the form of β-dicalcium silicate. Further, mortar containing no tricalcium silicate but containing dicalcium silicate with tricalcium aluminate or $5CaO.3Al_2O_3$ is also unstable in sulphate solutions. Thus, high alumina cement, in order to be resistant to sulphates, should contain neither of these aluminates. This narrows the ideal composition of this type of cement to the extent that the silica should be present as β-dicalcium silicate and the alumina as either monocalcium aluminate or $3CaO.5Al_2O_3$ or both. The lower early strength obtained with mixtures of β-dicalcium silicate and $3CaO.5Al_2O_3$ suggests that monocalcium aluminate is preferable as the main constituent of high alumina cement. The tendency of lean sand mortars of $3CaO.5Al_2O_3$ to disintegrate on lengthy exposures to fresh water, which has been repeatedly observed in this laboratory, further confirms this view.

Summary

I.   *The Preparation of the Experimental Mortars*

Starting with three cements as basic mixtures, (1) tricalcium silicate, (2) β-dicalcium silicate, (3) a mixture of (1) and (2) in equal proportions, 20% of each of these was substituted by tricalcium aluminate, $5CaO.3Al_2O_3$, monocalcium aluminate, $3CaO.5Al_2O_3$, dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$, respectively. The resulting mixtures as well as the pure aluminates and silicates (including γ-dicalcium silicate) were used as cements in the preparation of sand mortars. (Mainly mortars containing 1 part of the cement and 10 parts of standard sand by weight but also some $1:7\frac{1}{2}$ and $1:5$ mortars were used). Cements obtained by the substitution of 20% of the basic cements 1 and 3 above by the four calcium aluminates gave $1:10$ mortars of good strength. Similar substitution by dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$ gave mortars which gained strength more slowly than was to be expected from the amount of tricalcium silicate present but continued to increase in strength for long periods of time. Mortars of β-dicalcium silicate and mixtures of the aluminates with this hardened rather slowly, while addition of 20% of dicalcium ferrite and $4CaO.Al_2O_3.Fe_2O_3$ gave a $1:10$ mortar of very low strength at the end of seven weeks. Sand mortars made with tricalcium aluminate fell to pieces a short time after being exposed to pure water. Sand mortars made of γ-dicalcium silicate hardened extremely slowly but after 10 weeks in the molds they could be handled, gained slightly in strength on storing in water and much faster when stored in sulphate solutions.

II.   *Action of the Sulphate Solutions on the Silicate Mortars*

All the mortars expand and disintegrate ultimately when exposed to solutions of magnesium sulphate, the rate of expansion increasing with the con-

centration of the solution. The order of decreasing rate of expansion of the 1:10 sand mortars was: β-dicalcium silicate, tricalcium silicate, γ-dicalcium silicate.

The expansion of the silicate mortars exposed to 0.15 M Na_2SO_4 and saturated calcium sulphate at the end of three years exposure differed only very slightly from that of similar mortars exposed to distilled water.

Exposure of the silicate mortars to solutions of sulphates at first causes a rapid increase in the tensile strength of the specimens. Later the strength falls off in the case of the mortar exposed to solutions of magnesium sulphate, but the decrease of tensile strength progresses much more slowly, and is less for corresponding linear expansion, than with mortars made from Portland cement. The tensile strength of 1:5 sand mortars stored in 0.15 M Na_2SO_4 was higher at the end of four years' exposure than that of similar mortars stored in distilled water.

III. *Action of the Sulphate Solutions on the Aluminate Mortars*

The 1:10 mortars expand and disintegrate very rapidly when exposed to any of the sulphate solutions. The rate of expansion decreases in the order: $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$.

The resistance of the mortars to sulphate action increases very rapidly with increased richness of mix, this being greatest for mortars made of monocalcium aluminate, so that these tend to become more resistant in the richer mixes than mortars made with the other aluminates.

The action of solutions of sodium sulphate proceeds mainly from the surface of the specimen inward, the disintegrated material sloughing off as the action progresses. The action of solutions of magnesium sulphate differs in this respect, the whole bar expanding rapidly and ultimately cracking to pieces.

IV. *Action of Sulphate Solutions on the Mortars made from Mixed Cements*

The rate of expansion of the 1:10 sand mortars containing the silicates with or without admixtures of the aluminates etc., when exposed to 0.15 M $MgSO_4$ decreases in the following order[*]:

80% C_3S + 20% C_3A (1)[†] > 80% C_3S + 20% C_5A_3 (1.1)
> 80% C_3S + 20% CA; 40% C_3S + 40% β-C_2S + 20% C_3A (1.2)
> 40% C_3S + 40% β-C_2S + 20% C_5A_3 (1.5) > 80% C_3S + 20% C_5A_3;
80% β-C_2S + 20% C_3A (1.6) > 40% C_3S + 40% β-C_2S + 20% CA (2.2)
> 40% C_3S + 40% β-C_2S + 20% C_3A_5 (2.4) > Portland cement[‡] (3)
> C_3S + 20% C_4AF (5.5) > 80% β-C_2S + 20% C_5A_3 (9) > 80% C_3S +
20% C_2F (10) > 100% β-C_2S (15) > 40% C_3S + 40% β-C_2S + 20%
C_4AF (17) > 100% C_3S (20) > 40% C_3S + 40% β-C_2S + 20% C_2F; 50%
C_3S + 50% β-C_2S (39) > 80% β-C_2S + 20% CA (40) > 80% β-C_2S + 20%
C_4AF (190)

The mortars made with the mixtures 80% β-C_2S + 20% C_3A_5 and 80% β-C_2S + 20% C_2F are not classified.

Starting with the most rapidly expanding mortar and representing arbitrarily the time necessary for a linear expansion of 0.80% as unity, the numerals in brackets represent on the same scale the time required for the same linear expansion of the other mortars.

†*Symbols used:* $C = CaO$; $S = SiO_2$; $A = Al_2O_3$; $F = Fe_2O_3$.

‡*Average value for eight commercial Portland cements manufactured in eight different plants.*

The mortars which expanded more rapidly than Portland cement mortars were similar to the latter in showing rapid loss in tensile strength during expansion. Those mortars which expanded more slowly than Portland cement mortars retained their strength remarkably well.

All the 1:10 mortars which expanded faster than Portland cement mortar in 0.15 M $MgSO_4$ also expanded faster in 0.15 M Na_2SO_4 and in saturated calcium sulphate. Of the mortars which expanded more slowly than the average for similar mortars of Portland cement only the one made with 80% C_3S + 20% C_4AF had expanded to disintegration at the end of three years' exposure to 0.15 M Na_2SO_4, the others having expanded less than 0.10% at that time. At the end of three years' exposure to the saturated solution of calcium sulphate the bars made with 80% C_3S + 20% C_4AF and 80% β-C_2S + 20% CA had reached an expansion of between 0.10 and 0.20%, the others having a linear expansion of less than 0.10%.

V.   *Application to Hydraulic Cements*

1.   All Portland cements high in lime and containing normal amounts of alumina have a low resistance to natural waters containing sulphates of magnesium, sodium or calcium. The higher the lime content of the cement (*i.e.* the higher the percentage of tricalcium silicate) the alumina remaining the same, the lower is the resistance of the cement to the action of the sulphates.

2.   In the case of Portland cements high in lime (high in tricalcium silicate in comparison to the β-dicalcium silicate present) the resistance to the action of sulphates can be increased by decreasing the percentage of alumina (reducing the amount of tricalcium aluminate) or increasing the percentage of ferric oxide (changing tricalcium aluminate to $4CaO.Al_2O_3.Fe_2O_3$) or by both of these simultaneously. The resistance cannot be increased to equal that possessed by the pure silicate mixture present in the cement.

3.   In the case of Portland cements low in lime (high in β-dicalcium silicate as compared with tricalcium silicate) the resistance to solutions of magnesium sulphate can be increased by the methods described in the preceding paragraph so that it becomes much higher than the resistance of the corresponding mixture of the pure silicates. While the resistance to solutions of sodium sulphate and calcium sulphate cannot be increased up to that of the silicate mixture, an extremely high resistance to these solutions can be obtained by this method.

4.   In practice the limit to which the resistance can be increased by the methods in paragraph (3) is determined by the requirements of early strength since high later strengths are obtained with such mixtures.

5.   High alumina cements, in order to have the highest resistance to the action of sulphate, should be of a composition which gives no aluminate higher in lime than monocalcium aluminate and the silica should be present as β-dicalcium silicate. The presence of a large quantity of the aluminate $3CaO.5Al_2O_3$ is probably not desirable on account of the lower strength and the action of water on this substance.

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A CONVENIENT RING MOULD FOR RUBBER TESTING[1]

By D. F. STEDMAN[2]

Abstract

A mould is described which permits the direct moulding of rubber in the form of test rings, which for convenience may be made of the same radial dimensions as standard Schopper rings, while the thickness of the ring may be varied according to the amount of rubber inserted in the mould. These moulds are particularly useful when either the rubber or compounding ingredients are limited in amount, as they permit utilization of the whole of a sample, and tests may be obtained on quite small quantities.

It is very frequently necessary, especially in connection with chemical work on rubber, to make tensile or other tests on very small samples, when the quantities of either the rubber or filler available are definitely limited. The mould described has been found very convenient in such cases, as the whole of a sample may be utilized, and a fairly good test made on as little as 1 gm. of rubber, giving two rings, each nearly 1 mm. thick. To obtain two rings with

FIG. 1. *Ring mould.*

a slab mould and Schopper dies requires 26 gm. of rubber, and only 11.4% of the material used is recovered in the form of test rings. Moulds of this type were used in tests on synthetic rubber recently described by Whitby and Katz (1).

The mould is adapted for use in an oil or wax vulcanizing bath, or in an autoclave, but is not suited for use in a press. Those at present in use are turned from cold rolled mild steel.
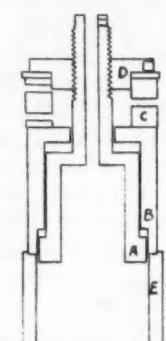
In Fig. 1, the mould is shown in vertical cross section. The rubber is enclosed between the flange on A, and the recess of B. It will be seen that only the radial dimensions of the test ring, which are conveniently the same as those of the regular Schopper ring, are fixed by the mould, the vertical dimension varying according to the amount of rubber inserted.

A is bored out to about the same thickness of metal as B, resulting in an equal rate of heating, and preventing the opening of any appreciable crack between the parts. If any such separation occurs the space is at once filled with rubber, giving a permanent fin. A very slight fin is of course always obtained, but if the external faces of A and the internal faces of B are fitted as accurately as possible and highly finished, such leakage of rubber is practically negligible.

As the rubber is forced over these faces when the mould is opened care must be used to prevent scratches on the surfaces. This danger would be eliminated if the moulds were hardened and ground, but the cost of such moulds would be

at least doubled. The moulds must also be cleaned very thoroughly after each use, and precautions taken against rusting, especially if chilled in cold water to stop the cure quickly.

In order to apply a definite and approximately known pressure to the rubber during cure a spring is used under the closing nut, giving about 750 lb. at 2 mm. compression. This spring must be designed very liberally in order to withstand the rather drastic treatment given by suddenly immersing in a vulcanizing bath. These springs have been increased in size considerably
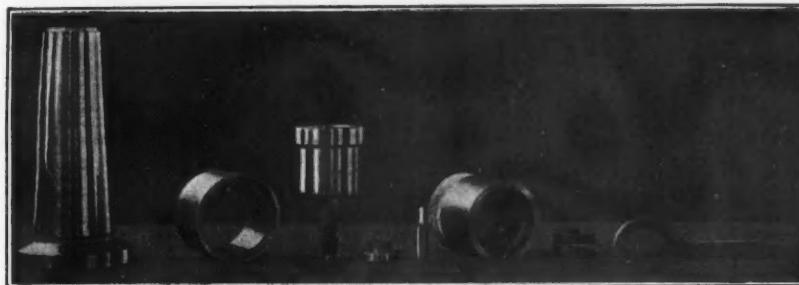
Fig. 2. *The parts of the ring mould.*

since the photograph (Fig. 2) was taken, and the dimensions suggested are $2\frac{1}{4}$ turns made from a square bar $\frac{1}{2}$ by $\frac{3}{4}$ in. wound on a former $1\frac{1}{2}$ in. in diameter, the first and last turns being ground flat to give even pressure. The recessed ring E is used to open the mould by gentle pressure in a small hydraulic press. The spanner shown on the right of the photograph is used to open the nut, the head of which carries an appropriate hole.

In designing the mould to give a particular size of ring it must be noted that the ring obtained is about 1.3% smaller than the diameter of the mould. A tapered mandrel has been found very useful in measuring the internal diameter of rings, as the shrinkage varies a trifle with different stocks.

The specimen of rubber is milled in the usual way to give a sheet free from air bubbles, and a strip cut just long enough to wrap round A immediately above the flange. The ends are butted together and joined firmly. Such a joint has shown no tendency to weakness, but to remove all suspicion the sheet may be milled out to a thickness of about 1 mm. and wrapped round under tension several times, avoiding air pockets, but with the materials so far tested no difference was detectable in the results obtained by both methods. When inserting a specimen of rubber in the mold it has also been found advantageous to apply and release the pressure several times to allow the escape of air.

It will be seen that the amount of rubber may be varied over wide limits and in fact for purposes of comparison rings have been made from 0.15 mm. to 7 mm. thick. Rings about 1 mm. thick give results only slightly lower than the maximum, while the optimum is at about 3 mm.

With these moulds a very slight "fin" is obtained on two edges, but this need not be removed completely as the dimensions are sufficiently uniform (to ± 0.01 mm.) that in most cases the fin need only be removed with a sharp pair of scissors from about 1 cm. of the ring.   As the entire fin weighs only a few mg. it may be neglected in a tensile test, and if the same weight of rubber is used in each of a set of moulds, variations in dimensions are not usually sufficient to require correction.

Reference

1. WHITBY, G. S. and KATZ, M.   Can. J. Research, 6: 398-408.   1932.

LIGNINS FROM CEREAL STRAWS

I. ISOLATION AND FRACTIONATION OF LIGNIN FROM OAT AND WHEAT STRAW[1]

By Léo Marion[2]

Abstract

The lignins isolated with methyl cellosolve (monomethyl ether of ethylene glycol) and concentrated hydrochloric acid, from both oat and wheat straw, have each been fractionated into five components by means of various solvents. The main fraction, soluble in acetone, which was isolated from oat-straw lignin has the same properties, methoxyl content and ultimate composition as the corresponding fraction of wheat-straw lignin. The components fractionated are compounds consisting of lignins combined with methyl cellosolve; lignins isolated by means of unmethylated solvents such as 1,4-dioxane have lower methoxyl values.

Plants belonging to families widely different from the Gramineae (Liliaceae, Compositae, Asclepiadaceae) gave rise through the identical process to lignins having different properties and composition than those isolated from straws.

Introduction

The quantitative isolation of lignin from cereal straws has been achieved hitherto only by the use of strong sulphuric acid (60-72%) or fuming hydrochloric acid, both methods destroying the non-ligneous part of the straw entirely. Dilute caustic soda, which has been used extensively, does not destroy the cellulosic material but removes less than half the lignin unless the extraction be run under pressure at higher temperatures. This method yields a product the solubility of which in organic liquids is negligible, and the purification of which is difficult and wasteful. It has been proposed to undertake a study of straw lignin with the purpose of investigating the properties of its sulphonic acids(sulphite liquors) especially in connection with tanning. To this end, the first object sought in the present work has been to isolate lignin in good yield from cereal straws by a process which, while removing the lignin in solution, would not destroy the cellulose and permit the recovery of the solvent. The action of 3% aqueous alkali at room temperature has not been found to give satisfactory results. A method which already had been applied by Fuchs (2) for the removal of lignin from spruce wood has been found remarkably suited to attain the object in view and also to yield a product having a relatively wide solubility range. As disclosed by this author the process involves the use of methyl cellosolve* containing 1% concentrated hydrochloric acid as catalyst. Neither catalyst nor solvent, however, is limited to those two substances and it is even advantageous to substitute 1,4-dioxane for methyl cellosolve as the former has a much lower boiling point and can therefore be reclaimed more readily. It has been found possible to separate the lignin obtained from both oat and wheat straw into fractions which are compared with the fractionation products of lignin isolated by Fuchs and Daur (3) from spruce wood.

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[1] *Manuscript received April 12, 1932.*
Contribution from the National Research Laboratories, Ottawa, Canada.
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*Monomethyl ether of ethylene glycol.

Oat straw, to which the process was applied first, was subjected to preliminary extractions with a methanol-benzene mixture to dissolve fats and resins (4-6%), and with water to remove the components (11-13%) soluble in that medium. The dried straw, containing 23.8% lignin, was then heated with methyl cellosolve containing 1 cc. of concentrated hydrochloric acid per 1000 cc. The residue, after washing and drying, was not as strongly colored as the initial material but still retained the structure of straw. It had lost about 40% of its weight and still contained 13-13.5% lignin. After removal of most of the methyl cellosolve by distillation under reduced pressure, the lignin was precipitated from the residual solution by the addition of water. Pentosans were removed by mild hydrolysis and the product left then represented a yield of 7-8% of the weight of straw, or about one-third of the total lignin present. It will be noted that a quantity of material appreciably greater than the yield of lignin has been removed, partly with the methyl cellosolve solution and partly during the subsequent washing of the residue with water. This discrepancy between the yield of lignin and the loss in weight of the material used has been observed previously in the isolation of lignin from spruce wood by the same process (2) and also in a very similar method in which use is made of methyl cellosolve containing a trace of dry hydrogen chloride (4). The pentosans present in the straw (about 15%) do not make up the total loss but the carbohydrates originally combined with the liberated lignin may form most of the remainder.

The extraction of oat straw with a 3% aqueous solution of sodium hydroxide yields a lignin which, before purification, may amount to 10% of the weight of straw but is lowered considerably by the latter process. This alkali-lignin was found to consist of two portions, one soluble and the other insoluble in 95% alcohol. The soluble fraction was further differentiated by a higher methoxyl content (16.87%) than the insoluble (14.94%). That the fractions, however, are probably not homogeneous is indicated by the fact that the product obtained from oat straw by means of methyl cellosolve and hydrochloric acid, which it is proposed to term oat-straw methylin*, can be fractionated. Oat-straw methylin is a brown amorphous powder, soluble in dilute alkali hydroxides from which it is precipitated by mineral acids but not by carbon dioxide; it therefore probably contains one or more free carboxyl groups. The actions of several solvents reveal its heterogeneous nature. Ether dissolves 7.5% which is soluble also in ethyl acetate, acetone, methanol and methyl cellosolve. Ethyl acetate dissolves 7.0%, insoluble in ether, but soluble in acetone, methanol, methyl cellosolve and chloroform. Acetone then removes a large fraction (52-53%) insoluble in ether and ethyl acetate but soluble in acetone, methanol and methyl cellosolve. A further fraction (14.6%) dissolved by methanol is insoluble in ether, ethyl acetate and acetone but soluble in methanol and methyl cellosolve. The residue, 17.5%, insoluble in ether, ethyl acetate, acetone, and methanol, is dissolved by methyl cellosolve. If this methyl cellosolve solution of the residue is allowed to dry spontaneously

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*Methylin is a word coined by W. Fuchs (3) to designate lignin which he had extracted from spruce-wood meal with methyl cellosolve containing concentrated hydrochloric acid.

the lignin is left as a lustrous dark resinous layer displaying a strong sheen; the resin, however, shrinks on drying further and becomes brittle. It will be noted from Table I that the composition of each of these fractions differs from the others and that the greatest divergence occurs between the extreme fractions.

Spruce-wood methylin has been separated by Fuchs and Daur (3) into four fractions, three soluble in ether, acetone, and chloroform respectively and a residue soluble in methyl cellosolve. These fractions differ from the oat-straw methylins both in methoxyl values and in properties. The former are insoluble in sodium carbonate solution whereas those fractions of oat-straw methylin which are soluble in solvents not miscible with water can be extracted with a 5% sodium carbonate solution.

The oat-straw methylins, with the possible exception of the ether-soluble fraction, do not consist of lignin as present in the straw, but of compounds in which the solvent is combined with the lignin. This apparently accounts for the methoxyl content of oat-straw methylin being so much higher (about 21-22%) than that of alkali lignin isolated from the same source (about 15-16%). In fact, this is demonstrated by a comparison of oat-straw methylin with a lignin isolated by the same process in which a non-methylated solvent such as 1,4-dioxane was substituted for the methyl cellosolve. Dioxane-lignin obtained from oat straw contains 13-14.5% methoxyl, a value which, remembering that dioxane-lignin contains combined dioxane, is very close to that of alkali-lignin. The effect of dioxane on straw is very similar to that of methyl cellosolve, and there is a marked discrepancy between the loss of weight of the straw, 36-38%, and the yield of lignin, 4-6%. That the product isolated from plant materials by the use of solvents of the foregoing type is a compound of the lignin and the solvent, has also been the conclusion reached previously by Fuchs (2), by Hibbert and Marion (4) and more recently by Rassow and Gabriel (5).

Attempts to isolate lignin from straw by means of methyl-cellosolve containing 0.05% of its weight of dry hydrogen chloride according to the method used by Hibbert and Marion (4) yielded but a small quantity of lignin (about 0.5 – 3.0%) which did not seem to possess more attractive properties than the methylin isolated when concentrated hydrochloric acid was substituted for the dry gas.

Wheat straw, when treated exactly as the oat straw with methyl cellosolve and acid, was found to yield an appreciably larger quantity of methylin than the latter. The yield amounted to 11-12% of the weight of straw employed. After the treatment, the residual straw was thoroughly washed with water and dried. Its weight in numerous experiments was always found to lie between 60-65% of the initial weight, and 13-15% of this was still lignin. The residue retained the structure of the original straw but had a less intense yellow color. Methylin obtained from wheat straw has the same physical appearance as oat-straw methylin and possesses much the same properties. It is soluble in dilute aqueous alkali hydroxides, producing brown solutions from which it is precipitated by mineral acids although not by carbon dioxide, indicating the possible presence of free carboxylic groups. As in the case of oat straw it has been

possible by means of solvents to separate this methylin into five fractions: an
ether-soluble fraction, about 8.2%, also soluble in ethyl acetate, acetone,
methanol and methyl cellosolve; a further 9.3% soluble in ethyl acetate,
acetone, methanol and methyl cellosolve, but insoluble in ether; a main fraction
soluble in acetone, methanol and methyl cellosolve, but insoluble in ether and
ethyl acetate and making up about 62.5% of the methylin; a small fraction,
4.2%, soluble in methanol and methyl cellosolve but insoluble in the first
three solvents; and a residue soluble in methyl cellosolve, insoluble in the other
solvents and amounting to 14.5% of the total.   These results are compared
in Table I with those obtained with oat-straw methylin.

TABLE I

FRACTIONS ISOLATED FROM OAT-STRAW AND WHEAT-STRAW METHYLINS

| | Oat straw | | | | Wheat straw | | | |
Fraction	Per cent of total methylin	% C	% H	% OCH₃	Per cent of total methylin	% C	% H	% OCH₃
Ether	7.5	67.86	7.96	13.94	8.2	65.68	7.21	18.60
Ethyl								
acetate	7.0	62.04	6.06	22.48	9.3	60.14	5.72	20.80
Acetone	52.6	60.74	5.92	22.19	62.5	60.61	6.05	21.68
Methanol	14.6	61.02	6.08	20.96	4.2	60.82	5.93	21.34
Residue	17.5	60.77	5.90	19.24	14.5	60.79	5.61	17.25

NOTE:—*The figures tabulated here have been averaged from the values reported in the experimental part.*

Table I emphasizes the similarity in composition between the acetone
fractions, obtained from oat-straw and wheat-straw methylins, and also
between the methanol fractions.   The members of any of the two pairs have
practically the same carbon and hydrogen content and the same methoxyl
values.   They all possess similar properties: they are very readily soluble in
dilute alkali hydroxides forming dark brown solutions from which carbon
dioxide fails to precipitate them.   Mineral acids added to these solutions
precipitate the methylin as colloidal suspensions which are coagulated by hot
water and then settle rapidly.   It will be noted that the methanol-soluble
fraction is obtained in much smaller yield from wheat-straw than from oat-
straw methylin.   The analytical figures of the two ethyl acetate-soluble frac-
tions present a noticeable divergence and the difference in the case of the ether
extracts is still wider so that comparison here precludes any idea of similarity.

On the basis of the foregoing results it can be concluded that both oat-
straw and wheat-straw methylins are heterogeneous mixtures, each separable
into at least five fractions possessing different physical properties and slightly
different chemical compositions.   Each mixture includes a predominating
fraction soluble in acetone and similar to each other in physical properties and
ultimate composition.   Different smaller amounts of a fraction soluble in
methanol are present which are also closely related.   These two fractions

are in each case mixed with varying quantities of substances with markedly different elementary composition. It is probable that these latter various components are responsible for the differences noted between the two methylins as isolated from each source. As none of the products isolated have been obtained in a crystalline form there is no definite criterion and therefore no certainty concerning the homogeneity of any of the fractions. Furthermore, the analytical figures of the acetone-soluble and methanol-soluble fractions of oat-straw methylin and those of the corresponding fractions of wheat-straw methylin differ by a negligibly small margin, although these fractions are known to be different. Hence, until further evidence has been accumulated it is not justifiable to regard these fractions as identical.

The fraction isolated from wheat-straw methylin, through its solubility in ethyl acetate, was methylated in chloroform solution with methyl iodide and silver oxide, its methoxyl content being raised from 20.80% to 33.68%, a value which as expected is higher than that found (30.2%) for lignin isolated from straw with alkalies (1)[*]. It is also much higher than that found by Fuchs (2) for spruce-wood methylin after exhaustive methylation (26.5%). Spruce-wood lignin is therefore quite different from that isolated from oat straw or wheat straw.

Lignin has also been isolated from various other sources. Plant materials belonging to families offering widely different characteristics such as *Senecio retrorsus*, a South African species, *Zygadenus venenosus* and the seed hairs of *Asclepias cornuti* (Decaisne) have been treated by the foregoing methods of isolation. The lignins and methylins obtained have been found to be a great deal different in properties and composition from those isolated from either oat or wheat straw. Lignin was isolated from *S. retrorsus* by three methods: (a) methyl cellosolve containing concentrated hydrochloric acid, (b) the same solvent and dry hydrogen chloride, and also (c) 3% aqueous sodium hydroxide. The yield was best with the last method but was always very much lower than with the straws. If the residue from the alkaline treatment after washing and drying was heated with methyl cellosolve and concentrated hydrochloric acid, the methylin obtained consisted almost entirely of a substance insoluble in sodium hydroxide whereas the methylin isolated from the original material— before alkaline treatment—was soluble. Methylin, then, may possibly consist of the compounds formed between methyl cellosolve and the lignin which is usually removed from the plant by dilute alkalies at room temperature and ordinary pressure. The methylin obtained from *S. retrorsus* has a very low methoxyl content (3.6%) and it has colloidal properties different from those of the straw methylins.

Zygadenus venenosus, a species belonging to the Liliaceae gives rise to a methylin which on precipitation from an alkaline solution forms very tenacious colloidal suspensions which it was not possible to coagulate completely. Its methoxyl content (2.94%) is remarkably low.

This value (30.2%) has been calculated from the molecular weight and hydroxyl content given by Beckmann, Liesche and Lehmann for their alkali-lignin.

From the seed hairs of *A. cornuti* (Decaisne), the common milkweed, a methylin was isolated as an amorphous, light-brown powder. It dissolves readily in dilute sodium hydroxide to form a dark-brown solution from which it is quantitatively precipitated by a stream of carbon dioxide. It does not therefore contain any free carboxylic group. Its methoxyl content (24.56%) is much higher than that of oat-straw or wheat-straw methylin. The suspensions which it forms on precipitation from its solutions are very easily coagulated. The various lignins and methylins obtained besides the straw methylins are listed in Table II together with their methoxyl content.

TABLE II

LIGNINS AND METHYLINS ISOLATED FROM VARIOUS PLANTS

Material	Method of isolation	% C	% H	% OCH₃
Oat straw	HCl (sp. gr. 1.2)	60.95	6.06	11.75
Oat straw (sol. in alc.)	3% NaOH	59.30	5.62	16.87
Oat straw (insol. in alc.)	3% NaOH	59.58	5.60	14.94
Oat straw	Glycol-HCl	60.72	6.22	16.98
Senecio retrorsus	3% NaOH	53.56	6.52	3.61
Zygadenus venenosus	Me.cellosolve and conc. HCl	—	—	2.94
Maple bark	Me.cellosolve and conc. HCl	—	—	12.96
Common milkweed seed hairs	Me.cellosolve and conc. HCl	61:01	6.53	24.56

A methylin, as seen from Table II, was also obtained from the bark of a maple tree. This product after a great deal of purification was found to have a methoxyl content of 12.96%. Its colloidal properties are quite pronounced and its coagulation offered some difficulty.

Methylins behave as true colloids and form suspensions the coagulation of which is most readily obtained in a slightly acid medium, *i.e.*, having a very low pH. It is noteworthy that with the methylins investigated there seems to exist a relationship between the ease of coagulation and the methoxyl content of the product. The milkweed methylin which has the highest methoxyl content was coagulated with the greatest ease; oat-straw and wheat-straw methylins have a methoxyl content but slightly lower and were coagulated with about equal readiness. The methylins isolated from *S. retrorsus* and from *Z. venenosus*, which both have unusually low methoxyl contents, were never completely coagulated no matter what method was tried. On the other hand bark methylin, which has a methoxyl content (12.96%) intermediate between the latter and that of the straw or milkweed methylins, was coagulated with considerably less difficulty than the products obtained from *S. retrorsus* or *Z. venenosus* although the task was much less readily achieved than in the case of the straw methylins.

Experimental

Preparation of Methylin from Oat Straw

Dry oat straw free from chaff was ground and extracted first with a minimum boiling-point mixture of methanol and benzene (loss 4.5 − 5.5%) and then with water (loss 11.7 − 12.7%). The residue was dried, mixed with ten times its

weight of methyl cellosolve and 10 cc. of concentrated hydrochloric acid per 100 gm. of straw and heated on the water-bath for three to four hours. The mixture was filtered while hot on a Buchner and washed with hot methyl cellosolve until the washings were clear. After a subsequent thorough washing with water, the residue was weighed; it had lost from 39-44% of its original weight and still contained 13.4% lignin (determined with 72% H_2SO_4). The combined filtrate and washings were distilled under reduced pressure to remove most of the methyl cellosolve and the residual liquor poured into a large volume of water. The precipitated methylin was washed by decantation with hot water, heated for some 30 min. with 2% hydrochloric acid, to hydrolyze the pentosans, and then washed again with hot water. The methylin was then dissolved by the addition of sodium hydroxide, the solution filtered and precipitated by the addition of dilute hydrochloric acid. The precipitate was washed six to seven times by decantation with hot water (80° C.), poured onto a Buchner, washed with hot water and dried in a current of air at 60° C. Yield 7.5%. The results of several preparations are given in Table III.

TABLE III
ISOLATION OF METHYLIN FROM OAT STRAW

Expt. No.	Wt. of straw, gm.	Residual straw		Yield of methylin		Duration of experiment, hr.
		Gm.	% Loss in wt.	Gm.	%	
1	96	54.2	43.5	7.3	7.6	4
2	213	129	39.5	17.7	8.4	3
3	202	115	43.1	16.0	7.9	5
4	250	147	41.2	17.4	7.0	4
5	520	312	40.0	40.0	7.7	5
6	260	—	—	21.3	8.2	4
7	2114	1278	39.5	153.4	7.2	4

The isolated methylin is an amorphous brown powder, soluble in dilute sodium hydroxide from which solution it is precipitated by dilute mineral acids but not by a stream of carbon dioxide. It is also soluble in methyl cellosolve, glycol and pyridine.

Fractionation of Oat-straw Methylin

Oat-straw methylin was extracted in a Soxhlet with ether, ethyl acetate, acetone and methanol successively, the material between extractions being warmed for several hours in a stream of air to remove the former solvent.

To purify each fraction the solvent was removed by distillation, the residue dissolved in sodium hydroxide, and the solution filtered and acidified with dilute hydrochloric acid. The precipitated material was washed several times by decantation with hot water and finally filtered, washed on the filter and dried.

The ether-soluble fraction (6.8, 8.2%) is a light yellow amorphous powder soluble in ether, ethyl acetate, acetone, methanol and methyl cellosolve. Analysis:— C, 67.94, 67.79%; H, 7.84, 8.08%; OCH_3, 14.08, 13.79%.

Ethyl acetate-soluble fraction (yield varied from 7-13%): light-brown amorphous powder insoluble in ether but soluble in ethyl acetate, acetone, methanol and methyl cellosolve. Analysis:— C, 62.13, 61.94%; H, 5.99, 6.14%; OCH₃, 22.28, 22.69%.

Acetone-soluble fraction (the yield varied, being as low as 35% and as high as 53%): very light-brown powder, insoluble in ether and ethyl acetate but soluble in acetone, methanol and methyl cellosolve. Analysis:— C. 60.74, 60.74%; H, 5.90, 5.95%; OCH₃, 22.13, 22.25%.

Methanol-soluble fraction (10.6, 10 7%): light-brown amorphous powder insoluble in ether, ethyl acetate, and acetone but soluble in methanol and methyl cellosolve. Analysis:— C, 61.06, 60.97%; H, 6.19, 5.97%; OCH₃, 21.04, 20.88%.

The residue left (17.5, 22.2%) is a brown amorphous powder still soluble in methyl cellosolve. Analysis:— C, 60.79, 60.75%; H, 5.90, 5.89%; OCH₃, 19.26, 19.23%.

Preparation of Dioxane-lignin from Oat Straw

In the preparation of lignin by the foregoing procedure it is possible to replace methyl cellosolve by another solvent of lower boiling point so that the recovery of solvent is easier. 1, 4-Dioxane is very suitable for this purpose and exactly the same procedure can be used as with methyl cellosolve. The loss in weight of the straw is 38% and the yield of dioxane-lignin 5.2% calculated on the initial weight of straw. The product is a light-brown amorphous powder. Analysis:— C, 61.42, 61.49%; H, 5.57, 5.58%; OCH₃, 14.32, 14.28%. Anhydrous aluminium chloride can be substituted for the hydrochloric acid but the yield is lower (3.8%) although the loss in weight of the straw is of the same order as previously (36%) and the product has not the same analytical figures as the former, C, 63.09%; H, 5.42%; OCH₃, 12.73%.

Glycol Ether Lignin from Oat Straw

This product was obtained by means of methyl cellosolve containing 0.05% of its weight of dry hydrogen chloride. The procedure followed was that described by Hibbert and Marion (4) for the treatment of spruce wood. The yield was always very low, varying from 0.5 − 3%. Previous to precipitating the lignin from the methyl cellosolve solution, the latter was allowed to cool and a yellowish-white substance deposited which was filtered. This was found to be soluble in hot alcohol but practically insoluble in the cold; it was not further investigated.

Alkali-lignin from Oat Straw

The procedure used was that of Beckmann, Liesche and Lehmann (1) *i.e.*, the action of 3% sodium hydroxide at room temperature. The solution was separated from the residual straw by means of the basket centrifuge. The lignin precipitated with dilute mineral acid from the impure solution was heated with 2% hydrochloric acid to remove the pentosans. It was then redissolved in dilute sodium hydroxide—an appreciable portion remaining undissolved—the solution filtered through a layer of kieselguhr and exactly

neutralized with dilute hydrochloric acid which caused the precipitation of silicic acid. This was filtered out and the filtrate acidified, the precipitated lignin being washed several times by decantation with hot water (80° C.). It coagulated and settled rapidly; it was filtered, washed with hot water and again filtered. The product, an amorphous light-brown powder, was stirred into alcohol and allowed to stand for several days, the flask being shaken occasionally. The insoluble was then filtered, washed with alcohol and dried. The alcoholic filtrate was treated with charcoal, reduced to a small volume and poured into water, the precipitated alcohol-soluble lignin being filtered, washed and dried. The yield after this purification process was only 2%. Analysis:–
(a) alcohol-soluble: C, 59.35, 59.25%; H, 5.72, 5.52%; OCH$_3$, 16.93, 16.81%.
(b) alcohol-insoluble: C, 59.56, 59.61%; H, 5.59, 5.62%; OCH$_3$, 14.97, 14.91%.

Preparation of Methylin from Wheat Straw

The ground straw was extracted with a 50% by volume methanol-benzene mixture (11.4% loss) and with water. The dried residue was then treated with methyl cellosolve and concentrated hydrochloric acid in exactly the same way as in the case of oat straw. The product was also purified just as in the last instance. In Table IV are given the results of a series of extractions in which various conditions have been used.

TABLE IV

ISOLATION OF METHYLIN FROM WHEAT STRAW

Expt. No.	Wt. of straw, gm.	Me Cellosolve, cc.	Catalyst	Residual straw			Yield of methylin		Duration of experiment, hr.
				Gm.	Loss in wt. %	Lignin content, %	Gm.	%	
1	206	1500	15 cc. conc. HCl	122	40.8	13.0	21.0	10.2	3.5
2	226	2000	20 cc. conc. HCl	130	42.5	—	24.8	10.9	4
3	42	440	4.5 cc. HAc	—	—	—	trace	—	2
4	194	1500	15 cc. conc. HCl	125	35.6	16.6	17.9	9.3	3.5
5	30	300	3 cc. H$_3$PO$_4$	—	—	14.4	—	—	2
6	203	2000	20 cc. conc. HCl	133	34.5	17.4	25.0	12.3	3
7	234	2000	20 cc. conc. HCl+5 cc. H$_3$PO$_4$	152	35.1	—	27.5	11.8	3.5
8	48	500	5 gm. hyd. AlCl$_3$	35	27.1	11.0	4.0	8.4	3
9	161	1600	15 gm. anhyd. AlCl$_3$	108	32.9	12.3	8.4	8.4	3.5

As will be noted in Experiments 8 and 9, the substitution of aluminium chloride, either hydrated or anhydrous, for the hydrochloric acid slightly lowered the yield. The use of acetic acid as catalyst was inefficient but phosphoric acid, although far less efficient than either hydrochloric acid or aluminium chloride, gave an appreciable yield. It had been hoped that phosphoric acid used along with the hydrochloric acid would facilitate coagulation of the precipitated methylin but it proved inefficient.

Fractionation of Wheat-straw Methylin

The fractionation was carried out exactly as for oat-straw methylin, the same solvents being used.

Ether-soluble fraction (9.9, 6.5%); a lemon-colored amorphous powder soluble in ether, ethyl acetate, acetone, methanol and methyl cellosolve. Analysis:- C, 65.70, 65.66%; H, 7.29, 7.13%; OCH_3, 18.61, 18.59%.

Ethyl acetate-soluble fraction (9.9, 9.1%); an amorphous, light-brown powder insoluble in ether but soluble in ethyl acetate, acetone, methanol and methyl cellosolve. Analysis:- C, 60.15, 60.12%; H, 5.75, 5.68%; OCH_3, 20.76, 20.85%.

Acetone-soluble fraction (62.6, 62.3%); a very light-brown amorphous powder insoluble in ether and ethyl acetate but soluble in acetone, methanol and methyl cellosolve. Analysis:- C, 60.53, 60.69%; H, 6.09, 6.01%; OCH_3, 21.81, 21.54%.

Methanol-soluble fraction (4.4, 4.0%); a light-brown amorphous powder insoluble in ether, ethyl acetate and acetone but soluble in methanol and methyl cellosolve. Analysis:- C, 60.64, 61.00%; H, 5.93, 5.93%; OCH_3, 21.24, 21.43%.

The residue left is a brown amorphous powder still soluble in methyl cellosolve. The methyl cellosolve solution on slow drying leaves a brittle, lustrous resinous mass. Analysis: C, 60.84, 60.74%; H, 5.63, 5.59 ; OCH_3, 17.03, 17.46%.

Methylation of Wheat-straw Methylin

The wheat-straw methylin soluble in ethyl acetate was dissolved in chloroform and the solution, mixed with equal weights of methyl iodide and silver oxide, was kept under reflux at 40° C. overnight. The mixture was filtered, the filtrate evaporated to dryness and the residue taken up in methyl cellosolve. After a treatment with charcoal the methyl cellosolve solution was poured into water and the precipitated product washed by decantation and on the filter with hot water and dried. It is a very light-brown amorphous powder. Analysis:- C, 62.27, 62.28%; H, 6.43, 6.43%; OCH_3, 33.84, 33.53%.

Preparation of Methylin from S. retrorsus

S. retrorsus is a shrub belonging to the Compositae and imported from South Africa. It was dried, ground, defatted with petroleum ether and extracted successively with methanol, benzene and water. The dried residue was then treated with methyl cellosolve and hydrochloric acid exactly as in the case of oat straw. As precipitated from its alkaline solution, however, the product was so fine that it ran through the filter. Neither heating nor the addition of aluminium sulphate could cause complete coagulation and settling, so the supernatant liquor containing very finely divided methylin in suspension was discarded. The loss in weight of the material was only 17.4%.

Alkali-lignin from S. retrorsus

The procedure followed here was exactly like that already described for oat straw. The product is a dark-brown powder soluble in alkali hydroxides. Analysis:- OCH_3, 2.89, 3.73 %. The residue left from the alkaline treatment,

after thorough washing and drying, gave rise, when heated with methyl cellosolve and hydrochloric acid, to a heterogeneous product the greater part of which was insoluble in dilute sodium hydroxide; it was not further examined.

Methylin from Z. venenosus

This plant which belongs to the Liliaceae was treated exactly as *S. retrorsus*. It suffered a loss in weight of 24% and yielded 1.7% of methylin. This product is a very dark-brown amorphous powder which throughout the procedure remained in a very finely divided state, which accounts for the very low yield obtained. Analysis:– OCH_3, 2.87, 3.00%.

Isolation of Methylin from Maple Bark

The dry bark of an old tree was crushed and ground to a powder. It was then defatted with petroleum ether (2%), extracted with methanol-benzene mixture (loss, 6.1%) and then with water. The product, which contained 35.1% lignin (determined by means of 72% H_2SO_4) was treated with methyl cellosolve and hydrochloric acid according to the procedure already described. This methylin (yield 9.5%) is a reddish amorphous powder, soluble in sodium hydroxide from which solution it is precipitated by mineral acids. Analysis:– OCH_3, 12.86, 13.07%. The product had to be washed with a large quantity of hot water in order to remove completely a soluble red substance.

Methylin from the Seed Hairs of the Common Milkweed

The seed hairs from the common milkweed (*A. cornuti*) were extracted with petroleum ether, a mixture of methanol-benzene and finally with water prior to being treated with methyl cellosolve and hydrochloric acid. The product, a light-brown amorphous powder, is soluble in dilute sodium hydroxide from which solution it is completely precipitated by a stream of carbon dioxide. Analysis:– OCH_3, 24.57, 24.54%.

Acknowledgment

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THE DETERMINATION OF MOISTURE IN HONEY[1]

By H. D. Chataway[2]

Abstract

The relationships between refractive index and moisture content of honey and between viscosity and moisture content have been quantitatively investigated, and as a result it has been found possible to utilize each of these properties for the determination of the moisture content. The requisite tables have been drawn up and details of the methods given. The degree of accuracy attainable is equal to that of the standard A.O.A.C. method, while the procedure is in both cases simpler and more rapid.

Introduction

In tne analysis of honey the determination of moisture content has always occupied a foremost place. Not only does moisture determine the consistency and to that extent the general quality of the honey, but it is also of importance in the question of fermentation (2, 5). Nevertheless the methods employed have long been regarded as unsatisfactory.

On the one hand there is the standard A.O.A.C. method which, on account of the time and attention to detail required, is suitable only for theoretical work. Moreover the results so obtained stand alone, unsupported by other evidence, and in consequence doubt often arises as to their accuracy (3). On the other hand practical men resort almost entirely to some form of honey hydrometer, and grade honey according to degrees Baumé. Because of the high viscosity of honey the determinations are usually made between 120° and 140° F., (49° C.—60° C.), but even then they are of very uncertain accuracy.

Intermediate between the absolute and the hydrometer methods is that based on refractive indices. Unfortunately the only tables available for the conversion of refractive index readings into per cent moisture have been those to be found in sugar handbooks. When applied to honeys these give results which are nearly 2% too high in moisture, in all probability because the refractive indices of cane sugar and of invert sugar differ considerably (4). As a result, the value of the refractometric method has been unduly discredited, in addition to the fact that its general use has been discouraged by considerations of expense.

The object of the present investigation was to discover, if possible, a method which should be both rapid and accurate and which should not involve the use of an expensive instrument. From the outset the hope was entertained that this might be accomplished by means of viscosity measurements. Since it was evident that a considerable number of honey samples would have to be analyzed for moisture by the standard method, a somewhat lengthy procedure, it was decided to carry on a study of the refractive index method at the same time, making use of the same samples.

Both lines of work have proved successful. The viscosity of honey has been found to be very sensitive to moisture content, a difference of 0.1% in the

latter giving rise to differences in viscosity ranging from 4 to 6%. The decrease in viscosity per unit increase in moisture content depends upon the temperature and also upon the moisture content itself. However, tables have been drawn up which take full account of these factors, and make it possible to calculate rapidly the moisture content of any honey given the time of fall of a standard steel ball at any observed room temperature.

The refractive index of honey is likewise found to give an accurate indication of moisture content. The ordinary sugar tables, however, must not be used. Instead a special honey table has been drawn up on the basis of the present work, and by its use correct moisture figures are obtained.

Experimental

Preliminary Viscosity and Refractive Index Measurements

The arbitrary viscosities at 25° C. of a limited number of honey samples were determined by the falling-ball method, while at the same time the refractive indices were taken. The refractive indices were plotted against the logarithms of the viscosities, and both refractive index and log viscosity were plotted against the absolute moistures as determined by the standard A.O.A.C. method. The curves obtained were almost straight lines, the individual points lying close to the lines. Moreover the correspondence was as good in the log viscosity-refractive index curve as in the other two curves. Since these preliminary experiments proved satisfactory a systematic study of the viscosity and refractive index properties of honey was undertaken.

Temperature Corrections Determined

(*a*) *Correction of refractometer reading.* The first step was to determine temperature corrections in order that readings might be taken at room temperature and the necessity of accurate and tedious temperature control eliminated. The correction per degree Centigrade proved to be independent of the temperature and of the moisture content of the honey. Thus, using the Pulfrich refractometer, in the case of two honeys having moisture contents of 18.2 and 14.5%, the change in refractive index between 15° C. and 25° C. was accurately linear and equal to $-.000232$ and $-.000223$ per degree respectively. Within experimental error, therefore, the temperature correction may be taken as $-.00023$ per degree Centigrade.

(*b*) *Corrections of viscosity.* In the case of the viscosity correction, however, much greater difficulty was encountered, for it was found that the correction per degree Centigrade varied slightly, not only with the temperature, but also with the moisture content of the honey. As a starting point, therefore, the viscosity-temperature relationships of a series of representative honeys were carefully determined.

For this purpose a jacketed glass tube was used, about 18 cm. long and 16 mm. in internal diameter (Fig. 1). A small glass tube, just slightly larger in diameter than the steel ball-bearing the time of fall of which was to be determined,
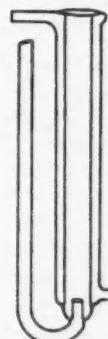
FIG. 1. *Apparatus used for determining viscosities of honey at different temperatures.*

projected for about 8 mm. of its length within the closed end of the jacketed tube.   In order to facilitate washing and thorough drying, the external end of this small tube was closed with rubber tubing and a glass stopper.

In carrying out a determination the apparatus was filled with honey, the steel ball introduced and the open ends corked.   The temperature of the honey was then carefully adjusted by passing through the jacket a constant stream of water of the exact temperature desired.   At the same time the steel ball was guided into the small tube through which it moved slowly due to the fact that the tube was only slightly larger in diameter than the ball.   The apparatus was then inverted and the delay which occurred before the ball left the small tube allowed all final adjustments of temperature, position of the tube, etc., to be made without haste.   In certain cases where more time was needed, the ball was held at the bend in the small tube by means of a magnet suspended above it.   The time of fall of the ball between two marks on the tube, 14 cm. apart, was then noted, using a stopwatch.   Table I shows a typical set of results obtained for one honey.

Similar sets of determinations were made for five other honeys of representative moisture contents.

TABLE I
TEMPERATURE-VISCOSITY READINGS FOR ONE HONEY

Temp., °C.	Time of fall, sec.	Temp., °C.	Time of fall, sec.
15	150.0	25	33.8
15	148.6	25	34.0
18	93.4	28	22.7
18	91.3	28	22.4
18	92.4	30	17.5
20	67.0	30	17.1
20	67.5	32	13.4
22	50.6	32	13.8
22	50.6	35	9.2
25	33.9	35	9.2

On plotting log viscosity against log absolute temperature, the graphs were found to be markedly non linear.   An endeavor was then made to find such a function $F(t, V_{25})$ that log viscosity plotted against log $F(t, V_{25})$ should be substantially linear, so that

$$\log V_t = M \log F(t, V_{25}). \tag{1}$$

It was found that $F(t, V_{25}) = 48 + t - .24 V_{25}$ fulfilled this condition very satisfactorily.

In any given case, over the range $t = 15°$ C. to $t = 30°$ C. the slopes of the lines were

$$M = \frac{\log V_{15} - \log V_{30}}{\log (48 + 15 - .24 V_{25}) - \log (48 + 30 - .24 V_{25})} \tag{2}$$

$$M = \frac{\log V_{15} - \log V_{30}}{\log \left[\dfrac{63 - .24 V_{25}}{78 - .24 V_{25}} \right]} \tag{3}$$

It was then found that, with a high degree of accuracy, for all the honeys

$$\log V_{15} - \log V_{30} = \frac{2.2 + \log V_{25}}{4}$$

whence

$$M = \frac{2.2 + \log V_{25}}{4 \log \left[\dfrac{63 - .24 \, V_{25}}{78 - .24 \, V_{25}} \right]} \tag{4}$$

It will now be seen that, from (1), (4),

$$\log V_{25} - \log V_t = M \left[\log(48 + 25 - .24 \, V_{25}) - \log(48 + t - .24 \, V_{25}) \right]$$

whence

$$\log \left(\frac{V_{25}}{V_t} \right) = \frac{(2.2 + \log V_{25})}{4 \log \left(\dfrac{63 - .24 V_{25}}{78 - .24 V_{25}} \right)} \log \frac{(73 - .24 \, V_{25})}{(t + 48 - .24 V_{25})} \tag{5}$$

from which the values of $\dfrac{V_{25}}{V_t}$ were computed.

This however, gives $\dfrac{V_{25}}{V_t}$ as a function of V_{25} and not as a function of V_t. Therefore, for a series of honeys, V_t was plotted as a function of t, and also the ratio $\dfrac{V_{25}}{V_t}$ as a function of t.

This gave two families of curves, from which, by interpolation of corresponding points between corresponding curves, $\dfrac{V_{25}}{V_t}$ was tabulated as a function of V_t, thus obtaining the desired correction factors.

Lastly, in order to eliminate any errors that might have crept in, the correction factors so obtained were themselves plotted and the final values were taken from smoothed curves. This, however made little difference in their values.

The final figures are given in Table II. In practice it is only necessary to multiply the observed time of fall at any temperature by the proper factor for that time and for that temperature, as found from this table, in order to obtain the time that would be required for the ball to fall the same distance through the honey at a temperature of 25° C.

As the preliminary experiments indicated, the logarithms of the time of fall, and of the refractive index are nearly proportional to the moisture content. It remained, therefore, to draw up tables showing the exact relationship of viscosity and refractive index, (both at a standard temperature—25° C.), to per cent of moisture.

Analysis of Samples

(a) *Methods*. As a basis for these tables some 60 honeys, collected from all parts of Canada and also from the United States, were examined. The viscosity, refractive index, and moisture content were determined at one time for each honey, in order to avoid any error due to possible changes in the honeys.

The procedure followed for the determination of viscosity was as simple as possible, the aim being to carry out the test exactly as it would be done in routine work, except that check determinations were made in all cases.

TABLE II

TEMPERATURE CORRECTION FACTORS FOR HONEY VISCOSITY MEASUREMENTS

Time of fall, sec.	Temperature, °C.																											Time of fall, sec.
	15.0	15.2	15.4	15.6	15.8	16.0	16.2	16.4	16.6	16.8	17.0	17.2	17.4	17.6	17.8	18.0	18.2	18.4	18.6	18.8	19.0	19.2	19.4	19.6	19.8	20.0	20.2	
10.0	305	313	322	330	338	346	354	363	373	382	390	399	414	423	432	442	451	462	472	484	495	507	517	536	550	564	577	10.0
12.5	301	310	317	325	333	341	351	360	369	377	386	395	408	417	427	437	447	458	468	480	491	503	515	531	544	557	571	12.5
15.0	298	306	314	322	330	338	347	356	365	373	383	391	404	412	423	433	442	453	464	475	486	497	510	527	540	552	565	15.0
17.5													401	408	419	429	439	449	460	470	482	493	505	520	534	545	559	17.5
20.0																								515	530	540	554	20.0
25.0	293	298	306	313	321	329	338	348	358	367	375	381	391	399	409	420	429	439	448	458	472	483	493	506	521	531	546	25.0
30.0	287	292	300	307	316	323	331	341	350	358	366	373	383	392	401	413	422	433	441	452	465	476	486	499	513	525	539	30.0
35.0	282	288	295	302	311	317	324	334	343	351	358	366	376	386	395	407	416	428	435	446	458	470	480	493	507	519	533	35.0
40.0	277	283	291	298	306	312	319	329	337	345	354	360	371	380	389	401	410	422	430	441	452	464	475	488	501	513	528	40.0
50.0	269	275	282	289	298	303	310	320	327	336	344	350	361	371	380	391	400	413	421	433	443	455	467	478	492	504	519	50.0
60.0	262	268	275	282	290	296	303	313	319	328	336	343	353	363	372	383	392	405	413	425	435	448	459	471	484	497	511	60.0
70.0	256	263	269	276	284	290	297	305	312	321	329	337	347	357	366	376	386	398	407	418	428	441	453	466	478	491	509	70.0
80.0	251	257	264	271	278	284	291	300	307	316	324	331	341	351	360	369	380	392	401	412	423	435	447	460	473	485	500	80.0
90.0	246	253	259	266	273	279	287	295	302	311	319	326	336	346	355	364	375	387	397	407	418	430	442	456	468	481	495	90.0
100.0	242	248	255	262	268	275	283	291	297	306	314	322	332	342	351	360	371	382	392	403	414	426	438	452	464	477	491	100.0
110.0	239	245	251	257	264	271	279	287	294	302	310	318	328	338	347	356	367	378	388	399	410	422	434	448	461	473	488	110.0
120.0	235	241	247	254	261	268	275	284	291	299	307	315	325	334	344	353	364	375	385	396	407	419	431	445	457	470	485	120.0
140.0	229	236	241	248	255	262	269	278	285	293	301	309	319	328	338	347	356	368	379	390	401	413	425	439	452	465	479	140.0
160.0	225	231	236	243	250	257	264	273	280	288	296	304	314	323	333	342	353	363	374	385	397	408	420	434	448	460	475	160.0
180.0	221	226	232	239	246	253	260	268	276	283	292	300	309	318	328	338	348	359	370	381	393	404	416	430	444	456	471	180.0
200.0	217	223	228	235	242	249	256	264	272	280	288	297	306	315	325	334	344	355	366	378	389	400	413	426	440	453	468	200.0
240.0	212	217	222	229	236	243	250	258	266	274	282	290	299	308	318	327	338	348	360	371	383	394	407	419	436	448	462	240.0
280.0	207	212	218	224	231	238	245	252	260	269	277	284	294	303	312	321	332	343	354	366	377	389	402	414	428	443	458	280.0
320.0	202	208	213	220	224	233	241	248	256	264	273	279	289	298	307	316	328	339	349	362	372	385	398	411	424	439	454	320.0
380.0	197	203	208	214	220	227	234	242	250	257	267	274	282	291	301	310	322	333	344	356	368	380	394	406	421	436	452	380.0
440.0	192	197	203	209	215	223	229	236	244	252	261	269	277	286	296	306	317	328	340	352	364	377	391	403	418	435	449	440.0
500.0	187	193	199	205	210	217	224	231	239	247	257	264	272	282	292	302	313	324	337	348	361	374	389	402	415	433	448	500.0
600.0	180	186	193	199	205	211	218	224	233	241	250	257	266	276	286	297	308	320	332	344	357	369	384	398	413	432	447	600.0
700.0	175	181	187	194	200	206	212	219	227	235	243	251	260	271	282	293	304	314	329	341	354	367	382	397	412	431	446	700.0
800.0	168	175	182	189	195	201	207	214	221	228	237	246	255	267	278	289	301	310	327	339	350	365	382	396	412	430	446	800.0
1000.0	161	167	174	181	186	192	199	206	212	221	230	239	248	261	272	284	297		324	337		364						1000.0
1200.0	154	160	167	173	180	186	191	198	207	215	225	235	245	258	271	283	296											1200.0
1400.0	151	157	163	171	177	183	189	196	204	214	224																	1400.0

TABLE II—*Continued*

Temperature in °C.

Time of fall, sec.	20.4	20.6	20.8	21.0	21.2	21.4	21.6	21.8	22.0	22.2	22.4	22.6	22.8	23.0	23.2	23.4	23.6	23.8	24.0	24.2	24.4	24.6	24.8	25.0	25.2	25.4	Time of fall, sec.
2.5																										1.045	2.5
5.0																		.875	.894	.915	.935	.955	.977	1.000	1.022	1.046	5.0
7.5							.688	.704	.718	.735	.750	.768	.784	.801	.818	.833	.851	.872	.892	.913	.933	.955	.976	1.000	1.023	1.047	7.5
10.0	.590	.605	.617	.633	.647	.662	.677	.694	.709	.725	.742	.758	.777	.793	.811	.829	.848	.869	.889	.911	.932	.954	.976	1.000	1.024	1.048	10.0
12.5	.584	.598	.612	.626	.641	.657	.672	.688	.704	.721	.737	.754	.771	.789	.808	.826	.845	.866	.887	.909	.931	.953	.975	1.000	1.025	1.049	12.5
15.0	.579	.593	.607	.622	.636	.651	.667	.682	.699	.715	.733	.751	.766	.785	.802	.823	.843	.863	.885	.907	.930	.952	.975	1.000	1.025	1.050	15.0
17.5	.574	.586	.600	.615	.629	.644	.660	.676	.693	.709	.727	.746	.762	.782	.799	.820	.840	.862	.883	.906	.928	.951	.975	1.000	1.026	1.051	17.5
20.0	.569	.582	.595	.610	.625	.640	.655	.671	.688	.705	.724	.743	.759	.779	.797	.818	.838	.860	.882	.904	.927	.950	.974	1.000	1.026	1.051	20.0
25.0	.561	.574	.587	.600	.617	.632	.648	.664	.681	.698	.717	.736	.753	.773	.792	.813	.834	.856	.878	.901	.926	.949	.974	1.000	1.027	1.053	25.0
30.0	.554	.566	.580	.594	.611	.626	.641	.658	.676	.693	.711	.730	.748	.769	.788	.809	.831	.853	.876	.899	.924	.948	.973	1.000	1.027	1.054	30.0
35.0	.548	.560	.574	.588	.605	.620	.636	.653	.671	.688	.707	.726	.744	.765	.785	.806	.828	.850	.874	.897	.922	.947	.973	1.000	1.028	1.055	35.0
40.0	.542	.556	.569	.584	.600	.616	.631	.649	.667	.684	.702	.722	.740	.762	.782	.803	.825	.848	.871	.895	.921	.946	.972	1.000	1.028	1.056	40.0
50.0	.532	.547	.561	.576	.592	.608	.624	.642	.660	.678	.695	.715	.734	.756	.777	.798	.820	.845	.868	.892	.918	.944	.971	1.000	1.029	1.057	50.0
60.0	.524	.540	.554	.569	.585	.601	.617	.635	.654	.672	.689	.710	.730	.752	.773	.795	.817	.842	.866	.889	.916	.943	.971	1.000	1.030	1.058	60.0
70.0	.518	.534	.548	.563	.579	.596	.612	.630	.649	.667	.685	.706	.726	.748	.770	.792	.814	.839	.863	.888	.915	.942	.970	1.000	1.030	1.060	70.0
80.0	.513	.528	.543	.559	.575	.591	.607	.626	.645	.664	.681	.702	.722	.745	.767	.789	.812	.838	.862	.886	.914	.941	.970	1.000	1.031	1.061	80.0
90.0	.509	.524	.538	.555	.571	.587	.603	.622	.642	.660	.678	.699	.719	.742	.764	.787	.810	.836	.860	.885	.913	.940	.970	1.000	1.031	1.062	90.0
100.0	.505	.520	.535	.551	.567	.583	.600	.619	.638	.657	.676	.697	.717	.740	.763	.785	.808	.835	.859	.885	.912	.940	.969	1.000	1.031	1.062	100.0
110.0	.502	.516	.531	.547	.563	.580	.598	.616	.636	.655	.674	.695	.715	.738	.761	.784	.807	.834	.858	.884	.911	.939	.969	1.000	1.032	1.063	110.0
120.0	.499	.513	.528	.544	.561	.577	.595	.613	.633	.652	.672	.693	.713	.736	.760	.783	.806	.833	.857	.884	.910	.939	.969	1.000	1.032	1.063	120.0
140.0	.493	.508	.523	.540	.555	.573	.591	.609	.629	.649	.669	.690	.710	.734	.758	.781	.804	.832	.856	.883	.910	.938	.970	1.000	1.032	1.063	140.0
160.0	.489	.504	.519	.536	.551	.569	.588	.605	.626	.645	.666	.688	.709	.732	.757	.780	.803	.831	.856	.883	.910	.938	.970	1.000	1.031	1.062	160.0
180.0	.485	.500	.515	.532	.548	.566	.586	.603	.624	.643	.664	.687	.707	.731	.757	.779	.803	.830	.856	.883	.909	.938	.970	1.000	1.030	1.062	180.0
200.0	.482	.497	.512	.530	.546	.564	.584	.601	.622	.641	.663	.686	.707	.730	.756	.779	.803	.830	.856	.884	.908	.938	.970	1.000	1.029	1.060	200.0
240.0	.476	.492	.508	.526	.542	.560	.581	.599	.620	.638	.661	.685	.707	.730	.757	.780	.804	.831	.857	.884	.909	.938	.970	1.000	1.026	1.057	240.0
280.0	.472	.488	.504	.524	.540	.558	.580	.599	.618	.637	.662	.686	.710	.734	.758	.784	.809	.833	.858	.884	.909	.939	.971	1.000	1.022	1.053	280.0
320.0	.470	.487	.502	.522	.539	.558	.580	.600	.621	.639	.664	.691	.716	.741	.767	.790	.816	.838	.861	.886	.911	.941	.972	1.000	1.017	1.048	320.0
380.0	.467	.485	.502	.523	.540	.559	.583	.604	.627	.642	.674	.704	.734	.760	.784	.803	.831	.848	.868	.890	.914	.945	.973	1.000			380.0
440.0	.465	.484	.501	.524	.542	.563	.589	.612	.637	.663	.692	.729	.762	.789	.812	.831	.848										440.0
500.0	.464	.483	.502	.526	.545	.569	.592	.623	.652	.682	.718	.761															500.0
600.0	.463	.483	.502	.532	.554	.584	.616	.649																			600.0
700.0	.464	.484	.504	.541	.569																						700.0
800.0	.465	.486	.509																								800.0

TABLE II—*Continued*

Temperature in °C.

Time of fall, sec.	25.6	25.8	26.0	26.2	26.4	26.6	26.8	27.0	27.2	27.4	27.6	27.8	28.0	28.2	28.4	28.6	28.8	29.0	29.2	29.4	29.6	29.8	30.0	Time of fall, sec.
2.5	1.070	1.080	1.110	1.134	1.158	1.183	1.206	1.232	1.257	1.283	1.310	1.340	1.367	1.398	1.430	1.460	1.493	1.526	1.560	1.597	1.633	1.670	1.706	2.5
5.0	1.072	1.088	1.113	1.140	1.164	1.191	1.219	1.248	1.276	1.305	1.335	1.363	1.395	1.427	1.460	1.493	1.528	1.564	1.600	1.637	1.674	1.711	1.748	5.0
7.5	1.073	1.093	1.119	1.146	1.172	1.200	1.229	1.260	1.289	1.320	1.351	1.382	1.416	1.453	1.483	1.520	1.558	1.594	1.633	1.675	1.716	1.756	1.796	7.5
10.0	1.075	1.098	1.124	1.151	1.180	1.208	1.239	1.270	1.301	1.330	1.365	1.398	1.434	1.471	1.507	1.544	1.582	1.622	1.663	1.707	1.749	1.795	1.839	10.0
12.5	1.076	1.101	1.128	1.155	1.186	1.214	1.246	1.277	1.310	1.343	1.377	1.412	1.450	1.488	1.524	1.564	1.606	1.649	1.688	1.733	1.779	1.826	1.875	12.5
15.0	1.078	1.103	1.132	1.159	1.191	1.220	1.252	1.283	1.318	1.352	1.387	1.423	1.462	1.502	1.540	1.580	1.622	1.668	1.708	1.754	1.806	1.853	1.901	15.0
17.5	1.079	1.106	1.135	1.163	1.195	1.225	1.258	1.289	1.324	1.360	1.396	1.433	1.473	1.514	1.554	1.595	1.637	1.684	1.725	1.772	1.825	1.875	1.926	17.5
20.0	1.080	1.108	1.137	1.166	1.199	1.229	1.263	1.294	1.330	1.367	1.404	1.442	1.482	1.525	1.565	1.607	1.649	1.698	1.740	1.787	1.842	1.895	1.945	20.0
25.0	1.082	1.111	1.142	1.171	1.204	1.236	1.271	1.304	1.341	1.379	1.417	1.457	1.498	1.542	1.583	1.626	1.671	1.720	1.765	1.813	1.868	1.926	1.976	25.0
30.0	1.083	1.114	1.145	1.175	1.209	1.241	1.277	1.312	1.350	1.388	1.428	1.468	1.510	1.555	1.597	1.643	1.688	1.737	1.785	1.834	1.891	1.946	2.000	30.0
35.0	1.085	1.116	1.148	1.179	1.213	1.246	1.283	1.317	1.358	1.397	1.436	1.478	1.521	1.566	1.609	1.656	1.701	1.751	1.801	1.851	1.908	1.966	2.018	35.0
40.0	1.086	1.118	1.150	1.182	1.217	1.250	1.288	1.324	1.364	1.403	1.443	1.486	1.530	1.574	1.618	1.668	1.712	1.763	1.814	1.866	1.921	1.980	2.034	40.0
50.0	1.088	1.121	1.153	1.187	1.222	1.256	1.295	1.331	1.373	1.413	1.454	1.499	1.543	1.588	1.633	1.684	1.730	1.780	1.834	1.888	1.940	1.998	2.054	50.0
60.0	1.090	1.123	1.156	1.191	1.226	1.261	1.300	1.338	1.379	1.421	1.462	1.507	1.552	1.597	1.643	1.693	1.741	1.793	1.846	1.897	1.950	2.003	2.059	60.0
70.0	1.092	1.124	1.158	1.194	1.229	1.264	1.304	1.343	1.384	1.426	1.468	1.512	1.557	1.602	1.647	1.696	1.743	1.796	1.845	1.894	1.948	1.997	2.052	70.0
80.0	1.092	1.126	1.160	1.196	1.231	1.267	1.307	1.347	1.387	1.428	1.471	1.514	1.558	1.602	1.647	1.694	1.738	1.789	1.839	1.885	1.936	1.984	2.033	80.0
90.0	1.093	1.126	1.161	1.197	1.233	1.269	1.308	1.349	1.388	1.429	1.471	1.513	1.557	1.600	1.644	1.689	1.729	1.779	1.827	1.871	1.918	1.962	2.009	90.0
100.0	1.093	1.127	1.161	1.198	1.233	1.270	1.309	1.350	1.387	1.428	1.470	1.510	1.553	1.595	1.637	1.679	1.717	1.765	1.811	1.852	1.895	1.932	1.977	100.0
110.0	1.094	1.127	1.161	1.198	1.233	1.270	1.308	1.349	1.386	1.425	1.466	1.505	1.547	1.587	1.625	1.666	1.700	1.747	1.789	1.827	1.868	1.900	1.937	110.0
120.0	1.094	1.127	1.161	1.198	1.233	1.269	1.307	1.346	1.383	1.421	1.461	1.499	1.538	1.576	1.611	1.650	1.680	1.726	1.763	1.798	1.837	1.866	1.897	120.0
140.0	1.093	1.126	1.159	1.196	1.230	1.266	1.303	1.340	1.372	1.408	1.443	1.477	1.511	1.546	1.574	1.608	1.624	1.665	1.703	1.732	1.768	1.785	1.804	140.0
160.0	1.092	1.124	1.157	1.192	1.224	1.259	1.295	1.330	1.355	1.388	1.416	1.446	1.473	1.500	1.522	1.540	1.560	1.587	1.627	1.656	1.705	1.718	1.725	160.0
180.0	1.092	1.122	1.153	1.187	1.216	1.248	1.284	1.317	1.334	1.361	1.381	1.409	1.427	1.449	1.462	1.480	1.500	1.520	1.540	1.575				180.0
200.0	1.089	1.119	1.137	1.180	1.206	1.236	1.277	1.298	1.308	1.328	1.353	1.373	1.390											200.0
240.0	1.085	1.113	1.137	1.161	1.182	1.191	1.218	1.245																240.0
280.0	1.080	1.106	1.125	1.141	1.156																			280.0
320.0	1.075	1.098																						320.0

Lengths of glass tubing approximately 25 cm. in length and 15 mm. inside diameter were used and on each a distance of 14 cm. was accurately marked off by file marks, 2 or 3 cm. being left at one end. This end was corked, the tube filled with liquefied honey and set up in an accurately vertical position. A thermometer graduated in $\frac{1}{10}°$ C. was clamped with its bulb accurately in the centre of the tube and about one inch below the surface of the honey. When the temperature of the honey had become reasonably constant, a steel ball-bearing ("S.K.F." $\frac{3}{16}$ in.) was dropped down the centre of the tube, its time of fall between the two marks being noted by means of a stopwatch. In the case of thin honeys the temperature was noted and the thermometer removed immediately before dropping the ball. In the case of thick honeys the ball was dropped down between the thermometer and the wall, and was then brought to the centre by tilting the tube before the ball reached the top mark. In these cases the temperature was noted when the ball passed the top and the bottom mark and the average temperature recorded. These precautions and the use of a sensitive thermometer are necessary since in general the accuracy of the method depends more upon the exactness of the temperature reading than upon anything else. Each reading was multiplied by its proper correction factor and the readings repeated until reasonably accurate checks for the viscosity at 25° C. were obtained.

The narrow tube is suitable for use where only small samples (3 oz. is quite sufficient) are available, and where liquefaction and subsequent cooling must be carried out fairly rapidly. Otherwise it would probably be more convenient to fill large graduated cylinders with the honey, allow them to come to constant temperature in a suitable room overnight, observing the time of fall in the morning. The need for carefully placing the tube in a strictly perpendicular position would thus be avoided, but on the other hand, following variations in room temperature, serious temperature gradients might develop between the different strata of the honey.

For the determinations of refractive indices a Zeiss industrial refractometer was used and found to be very convenient and satisfactory. The frequency with which results could be checked to closer than one in the fourth place justified estimating the readings to the fifth place and this was accordingly done. Readings were taken at room temperature and corrected to 25° C. on the basis of −.00023 per degree. The instrument was later checked against a Pulfrich and was found to give readings on the average .0003 too high. The observed readings were therefore corrected by this amount.

The determination of the moisture content was carried out by drying on sand in a vacuum oven according to the standard A.O.A.C. procedure. The dishes were in almost every case placed in the vacuum oven at 5.00 p.m. and removed for their first weighing next morning. They were then replaced and weighed for the second time early in the afternoon, when they generally showed a slight increase in weight, but not sufficient to invalidate the earlier reading. The work was done during the dry winter months, phosphorus pentoxide desiccators being used. Each determination was done in duplicate and the

results averaged. It is to be noted that in this particular case, the A.O.A.C. method cannot lead to any very great degree of accuracy since it directs that an amount of material shall be taken that will yield approximately 1 gm. of dry matter, and also that the heating shall be continued and weighings made every two hours until the difference between successive weighings is not more than 2 mg.
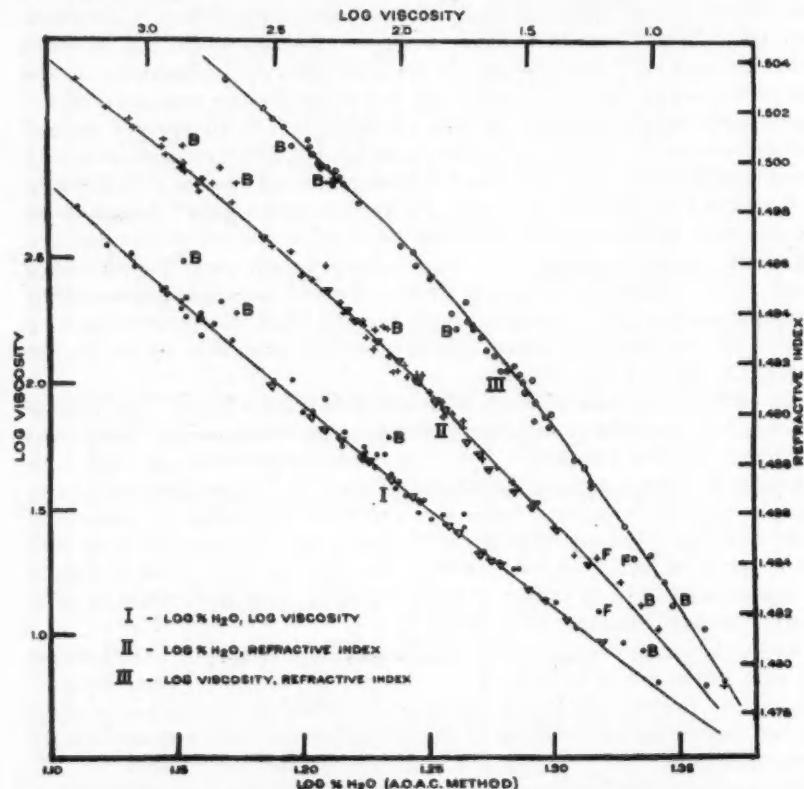
FIG. 2. *Results of viscosity, refractive index and A.O.A.C. moisture determinations, plotted to show the comparative accuracy of the results. The three points in the extreme lower right hand corner although not marked by the letter B were obtained from a buckwheat honey. Such honeys regularly give abnormal results.*

(*b*) *Results.* The results are shown in Fig. 2. In order to obtain lines which should be as straight as possible the co-ordinates chosen were: Curve I, log moisture-log viscosity; curve II, log moisture-refractive index and curve III, log viscosity-refractive index. The points which represent buckwheat honeys are specially designated by the letter *B*. These honeys show abnormally high viscosities and slightly less high refractive indices, judged by their moisture contents. The points designated *F* were obtained from a

TABLE III

DETERMINATION OF MOISTURE CONTENT FROM VISCOSITY AND REFRACTIVE INDEX* MEASUREMENTS

% H_2O	Time of fall through 14 cm., large ball, sec.	Refractive index at 25° C.	% H_2O	Time of fall through 14 cm., large ball, sec.	Refractive index at 25° C.	% H_2O	Time of fall through 14 cm. at 25° C., sec. — Large ball	Small ball	Refractive index at 25° C.	% H_2O	Time of fall through 14 cm. at 25° C., sec. — Large ball	Small ball	Refractive index at 25° C.
12.0	982	1.50550	14.6	164.8	1.49884	17.2	41.2		1.49234	19.9	12.65	30.3	1.48570
.1	906	529	.7	155.2	859	.3	39.1		210	20.0	12.16	29.1	548
.2	840	504	.8	145.9	832	.4	37.1		185	.1	11.70	28.0	526
.3	776	481	.9	137.7	807	.5	35.5		160	.2	11.25	26.9	503
.4	719	454	15.0	129.8	781	.6	33.7		134	.3	10.84	25.9	481
.5	668	427	.1	122.2	756	.7	32.2		108	.4	10.45	25.0	460
.6	618	401	.2	116.4	735	.8	30.8		083	.5	10.07	24.1	437
.7	575	374	.3	109.4	706	.9	29.4		057	.6	9.68	23.2	416
.8	535	346	.4	102.8	681	18.0	28.1		032	.7	9.33	22.3	394
.9	496	319	.5	97.5	657	.1	26.9		009	.8	9.03	21.6	373
13.0	462	293	.6	92.1	632	.2	25.7		1.48983	.9	8.69	20.8	352
.1	428	266	.7	87.5	607	.3	24.7		959	21.0	8.38	20.1	329
.2	400	240	.8	83.2	581	.4	23.6		935	.1	8.07	19.3	305
.3	374	219	.9	79.1	557	.5	22.6		909	.2	7.82	18.7	284
.4	348	189	16.0	75.0	533	.6	21.7		885	.3	7.53	18.02	261
.5	325	162	.1	70.8	507	.7	20.7	47.5	860	.4	7.28	17.42	240
.6	304	136	.2	67.4	482	.8	19.86	45.6	840	.5	7.03	16.82	217
.7	285	111	.3	63.6	457	.9	19.05	43.7	811	.6	6.76	16.18	195
.8	266	084	.4	60.7	431	19.0	18.28	42.0	786	.7	6.50	15.55	172
.9	251	061	.5	57.8	405	.1	17.54	40.2	762	.8	6.28	15.03	149
14.0	237.7	035	.6	54.8	382	.2	16.79	38.5	732	.9	6.10	14.60	127
.1	221.3	010	.7	52.1	357	.3	16.07	37.0	713	22.0	5.89	14.09	103
.2	208.4	1.49985	.8	50.0	333	.4	15.45	35.5	690	.1	5.72	13.69	080
.3	196.3	960	.9	47.5	307	.5	14.83	34.0	666	.2	5.50	13.16	056
.4	185.4	940	17.0	45.4	283	.6	14.22	32.7	641	.3	5.31	12.70	031
.5	174.2	910	.1	43.3	259	.7	13.65	31.5	618	.4	5.13	12.28	008
						.8	13.15		593	.5	4.95	11.84	1.47982

*Correction of refractive index = −0.00023 per °C.

sample of fermented honey. At first it was thought that all samples which had undergone even slight fermentation gave abnormal results, but this proved not to be the case. Just what effect serious fermentation has must be left an open question at present.

Superimposed upon Curves I and II are a number of points represented by triangles; these were not obtained from different honeys but by the dilution and concentration of only two samples. Since these points lie accurately upon the curves it is evident that the viscosity and refractive index of honeys which have been diluted and of those which are naturally thin do not differ appreciably.

Discussion

Explanation and Discussion of Tables III and IV

Curves I and II, Fig. 2, were used as the basis for Table III showing the relation between moisture content on the one hand and refractive index and viscosity on the other. In this table, the arbitrary values of viscosity which are used throughout this work are given in terms of the time of fall of a "large" and a "small" ball. These terms refer to steel ball-bearings $\frac{3}{16}$ and $\frac{3}{32}$ in. in diameter, respectively. The small ball should be used whenever possible in the testing of thin honeys since the experimental error in determining the longer time of fall is relatively less. The large balls actually used in this investigation were "S.K.F." ball-bearings weighing 0.4370 ± 0.0002 gm. A same sized "Hoffmann" ball-bearing weighed 0.4394 gm. It is probable, therefore, that the make of the steel ball is of no importance except in the most accurate work.

It will be seen that the "goodness of fit" is about the same for all methods, indicating that the limits of error characteristic of the individual determinations by each method are approximately the same.

Using Table III the actual moisture contents for the 60 honeys were calculated from the viscosity and refractive index figures which had been obtained and the results are shown in Table IV. The first group of honeys was supplied by the Bee Division, Central Experimental Farm, Ottawa, and consisted of a random selection from a collection of 211 honeys of the 1929 crop. Each sample had been analyzed by the Division of Chemistry (5, pp. 112-115) for moisture, ash, hydrogen ion concentration, titrateable acidity, nitrogen, invert sugar, sucrose, levulose, and dextrose. However no correlation could be discovered between these figures and the results of the present work.

The above samples were small ones, which during the course of time had lost several per cent of moisture and were thus of abnormally high viscosity. An effort was therefore made to obtain some honeys of higher moisture content, but none of very high moisture content could be found since the honey flow of 1931 had ceased before the lack of such honeys for investigation purposes was realized. The second group, however, represents moderately thin honeys supplied partly by the Dominion Apiarist and partly by the Ontario Honey Producers Co-operative, Ltd. The third group also consists of honeys of fairly high moisture content, being those most kindly sent by Mr. H. F. Wilson, Dept. of Economic Entomology, University of Wisconsin.

In the case of six honeys for which the results appeared to be abnormal and

TABLE IV
Moisture determinations on sixty honeys

No. of sample	A % water by A.O.A.C. method	B % water from ref. index	C % water from viscosity	A-B	A-C	B-C
Samples from Division of Bee Culture, Dominion Experimental Farm						
6	14.25	14.18	14.13	.07	.12	.05
10	13.61	13.60	13.67	.01	− .06	− .07
10a	13.96	13.91	14.02	.05	− .06	− .11
18	13.27	13.31	13.41	− .04	− .14	− .10
19	14.00	13.80	14.03	.20	− .03	− .23
24	14.26	14.29	14.41	− .03	− .15	− .12
32	14.02	14.04	14.08	− .02	− .06	− .04
39	14.63	14.50	14.54	.13	.09	− .04
67	15.44	15.47	15.42	.03	− .02	− .05
69	15.70	15.56	15.42	.14	.28	.14
79	14.74	14.26	14.21	.48	.53	.05
113B	14.95	14.50	14.38	.45	.57	.12
117	14.19	14.25	14.30	− .06	− .11	− .05
120	16.15	15.75	15.65	.40	.50	.10
121	18.33	18.21	18.12	.12	.21	.09
124	14.46	14.47	14.45	− .01	.01	.02
130	15.85	15.93	15.95	− .08	− .10	− .02
142	16.78	16.67	16.67	− .11	− .11	.00
143	16.93	17.04	16.96	− .11	− .03	.08
152	12.93	12.89	12.91	.04	.02	− .02
154	14.47	14.45	14.38	.02	.09	.07
158	14.88	14.80	14.77	.08	.11	.03
176	13.57	13.47	13.54	.10	.03	.07
183	14.42	14.42	14.47	.00	− .05	− .05
185	14.46	14.39	14.55	▼ .07	− .09	− .16
186B	23.35	22.80	21.73	.55	1.62	1.07
194B	14.24	13.90	13.61	.34	.63	.29
202	14.20	14.22	14.16	− .02	.04	− .06
Miscellaneous samples of higher moisture content						
1	18.19	18.16	18.20	.03	− .01	− .04
2	17.61	17.53	17.57	.08	.04	− .04
3	17.45	17.56	17.42	− .11	.03	− .04
4	18.70	18.88	18.69	− .18	.01	− .19
5	17.30	17.47	17.23	− .17	.07	.24
6	17.24	17.48	17.35	− .24	− .11	.13
7	17.70	17.54	17.58	.16	.12	− .04
8	16.42	16.36	16.56	.06	− .14	− .20
9	16.77	16.66	16.59	.11	.18	.07
10	17.17	17.23	17.12	− .05	.05	.10
11B	17.15	16.79	16.39	.36	.76	.40
12B	21.62	21.45	21.01	.17	.61	.44
13	18.88	18.99	18.92	− .11	− .04	.07
14F	20.77	20.58	20.05	.19	.72	.53
15	21.22	21.04	20.81	.18	.41	.23
16	20.35	20.52	20.44	− .17	− .09	.08
17	18.36	18.24	17.87	.12	.49	.37
18	18.04	18.18	18.10	− .14	− .06	.08

TABLE IV—*Continued*

No. of sample	A % water by A.O.A.C. method	B % water from ref. index	C % water from viscosity	A-B	A-C	B-C
American samples of high moisture content						
I	19.31	19.33	19.08	−.02	.23	.25
II	17.65	17.64	17.64	.01	.01	.00
III	17.42	17.34	17.49	.08	−.07	.15
IV	17.83	17.80	17.97	.03	−.14	−.17
V	16.47	16.52	16.31	−.05	.16	.21
VI	17.08	16.74	16.69	.34	.39	.05
VII	18.02	17.95	17.89	.07	.13	.06
VIII	19.96	20.01	19.84	−.05	.12	.17
IX	17.61	17.62	17.84	−.01	−.23	−.22
X	19.22	19.20	19.04	.02	.18	.16
XI	16.82	16.91	16.86	−.09	−.04	.05
XII	16.95	16.80	16.71	.15	.24	.09
XIII	16.00	15.99	15.97	.01	.03	.02
XIV	17.61	17.62	17.84	−.01	−.23	−.22

TABLE V

COMPARISON OF RESULTS OF AUERBACH AND BORRIES WITH THOSE
OBTAINED BY USE OF TABLE IV

Ref. index at 40° C. (A. and B.)	Ref. index corrected to 25° C.	% H_2O calculated by A. and B.	% H_2O calculated from Table IV	Difference
Normal honeys				
1.4938	1.4972	15.36	15.25	−.11
1.4906	1.4940	16.61	16.52	−.09
1.4904	1.4938	16.69	16.60	−.09
1.4917	1.4951	16.18	16.10	−.08
1.4882	1.4916	17.55	17.50	−.05
1.4906	1.4940	16.61	16.52	−.09
1.4863	1.4897	18.29	18.25	−.04
1.4855	1.4889	18.60	18.58	−.02
1.4829	1.4863	19.62	19.65	+.03
1.4811	1.4845	20.32	20.44	+.12
15-Year-old honeys				
1.4957	1.4991	14.62	14.50	−.12
1.4906	1.4940	16.61	16.52	−.11
1.4904	1.4938	16.69	16.61	−.08
1.4865	1.4899	18.21	18.17	−.04
1.4857	1.4891	18.52	18.50	−.02
1.4878	1.4912	17.70	17.65	−.05
1.4864	1.4898	18.25	18.21	−.04
Special honeys				
1.5017	1.5051	12.27	12.12	−.15
1.4984	1.5018	13.56	13.44	−.12
1.4882	1.4916	17.55	17.50	−.05
1.4969	1.5003	14.15	14.02	−.13
1.4994	1.5028	13.17	13.05	−.12
1.4741	1.4775	23.05		

therefore open to suspicion, the determinations were repeated, but, except in the case of two, the resulting corrections were negligible. It may safely be concluded, therefore, that the discrepancies in the recorded results are due, not so much to experimental error in technique, as to the theoretical limits of accuracy of the different methods.

Comparison with the Work of Auerbach and Borries

It is satisfactory to note the almost theoretical agreement between the refractive index results arrived at in this work and those obtained by Auerbach and Borries (1). These workers determined (a) the density to five places of decimals (using diluted samples and a pycnometer), (b) the refractive index at 40° C., and (c) the moisture content by a special drying method, of 10 honeys. From these results they deduced empirical equations for the relationships between refractive index, density and moisture. Using these equations they calculated, on the basis of both refractometric and density measurements, the moisture content of 23 honeys, seven of which they classified as 15-year-old honeys and six as "special honeys". Since in their paper they also published the actual refractive indices at 40° C. from which they made their calculations, it has been possible to check their calculations against those developed in the present investigation. A comparison of results is shown in Table V.

Hydrometer Method to be Investigated

Further, the work of Auerbach and Borries brings to the fore the question of the accuracy and suitability of the hydrometer. As will be seen from the last column, Table VI, the differences they obtained between moisture determined by density and moisture determined by refractive index are very small. True, the agreement between these and their absolute figures is not as good, but the considerably better agreement obtained between refractive index and absolute moisture determinations in the present work seems to show that the source of their discrepancies must lie at least partly in the moisture determinations themselves and not altogether in the indirect methods. However, their figures do show that density in itself is as accurate an indication of

FIG. 3. *Curves indicating the degree of accuracy at present obtainable by hydrometer methods on undiluted honeys.*

moisture content as is refractive index.

On the other hand the determination of the density of a diluted sample of

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TABLE VI

AUERBACH AND BORRIES' FIGURES FOR THE COMPARISON OF DIRECT
AND INDIRECT METHODS OF MOISTURE DETERMINATION

D	E	F	D-E	D-F	E-F
% water by direct weighing	% water from density	% water from ref. index			
Normal honeys					
15.71	15.49	15.36	0.22	0.35	0.13
15.80	16.43	16.61	−0.63	−0.81	−0.18
16.27	16.63	16.69	−0.36	−0.42	−0.06
16.46	16.13	16.18	0.33	0.28	−0.05
16.99	17.54	17.55	−0.55	−0.56	−0.01
17.27	16.59	16.61	0.68	0.66	−0.02
17.34	18.18	18.29	−0.84	−0.95	−0.11
19.11	18.66	18.60	0.45	0.51	0.06
19.83	19.48	19.62	0.35	0.21	−0.14
20.66	20.43	20.32	0.23	0.34	0.11
15-Year-old honeys					
15.03	14.76	14.62	0.27	0.41	0.14
16.37	16.72	16.61	−0.35	−0.24	0.11
16.95	16.85	16.69	0.10	0.26	0.16
17.63	18.24	18.21	−0.61	−0.58	0.03
17.75	18.57	18.52	−0.82	−0.77	0.05
18.15	17.93	17.70	0.22	0.45	0.23
18.53	18.39	18.25	0.14	0.28	0.14
Special honeys					
13.39	12.43	12.27	0.96	1.12	0.16
14.66	13.35	13.56	1.31	1.10	−0.21
17.94	17.60	17.55	0.34	0.39	0.05
15.67	14.35	14.15	1.32	1.52	0.20
13.03	13.10	13.17	−0.07	−0.14	−0.07
23.52	23.06	23.05	0.46	0.47	0.01

honey in a pycnometer bottle and the determination of the density of a heated undiluted honey sample using a hydrometer are two entirely different things. The first is accurate but is such a slow and delicate procedure as to be useless in practical work. The second method is simple and fairly rapid but the actual results obtained may be exceedingly poor. Thus, using a special honey hydrometer supplied by the Dominion Apiarist, and which was designed for testing small samples of honey, the results shown in curve I, Fig. 3 were obtained. As will be seen, the individual density determinations on one and the same sample vary by an amount corresponding to over 2% of moisture. For comparison, some results supplied by Mr. L. Skazin, of these Laboratories, obtained with the use of a larger and more sensitive instrument belonging to the Ontario Honey Producers Co-operative, Ltd., are shown in curve II, Fig. 3. As will be seen, these are decidedly better. However one of the drawbacks is that very much larger samples are required for testing purposes.

It will be seen that the whole question of the practical value of the hydro-

meter method depends upon whether or not it is possible to devise an instrument which will be accurate as well as convenient. Work will be undertaken along these lines.

In the meantime, one or two remarks may be made with reference to the question as to which of the two methods, viscosity or refractive index, is the more suited to practical work. Where the cost of the instrument is a matter of minor consideration, it is probable that the refractive index method is the more suitable because of the ease and rapidity with which readings can be made. However, great care should be taken to secure a representative sample and to take the readings with the utmost precision. On the other hand, the apparatus for the measurement of viscosity is much cheaper, a good thermometer and a stopwatch being practically all that is required. Further, the measurements may be carried out by a less skilled observer, especially if large samples sufficient to fill reasonably wide tubes are available.

Summary

(1) A new method for the determination of moisture in honey, one dependent on viscosity, has been studied and found practicable.

(2) Viscosity, refractive index, and absolute moisture determinations have been carried out on 60 honeys.

(3) Based upon the above figures, tables have been drawn up which make it possible to determine moisture content simply and rapidly, either from viscosity or from refractive index measurements, with an error in all probability no greater than that of the standard A.O.A.C. method. However, buckwheat honeys and possibly those which have become fermented, give abnormal results.

(4) The ground has been cleared by preliminary work for a study of the degree of accuracy obtainable with carefully designed honey hydrometers.

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THE EFFECT OF COOKED POTATO IN CONJUNCTION WITH FERMENTABLE CARBOHYDRATE IN BREADMAKING[1]

By R. H. Harris[2]

Abstract

A series of 11 flours of different types and baking strengths were baked by a variety of methods in order to determine the effect of adding fermentable sugar to the dough in conjunction with cooked white and sweet potato. Preliminary bakings using a simple formula of flour, water, yeast, and salt, with and without sucrose, indicated the value of sucrose in flours of low diastatic power.

The addition of cooked white potato in the absence of sucrose gave still poorer results with these low diastatic flours, but improved the better flours. The addition of sucrose increased the response of all flours, the maximum stimulation being obtained when both malt and sucrose were added. Evidently, cooked white potato is not a satisfactory substitute for fermentable sugars.

It was found that cooked sweet potato not only supported yeast activity, but also stimulated it. However, it also imparted a deleterious dark tint to the loaf, thus lowering the color score.

The addition of potassium bromate without sucrose resulted in a greater loaf volume than that obtained by the use of the simple formula with sucrose, except in the case of two flours, particularly low in diastatic activity. The inclusion of diastatic malt increased the loaf volumes of these two flours.

No significant relationship was found between protein content and loaf volume, in the absence of added fermentable carbohydrate. The addition of sucrose and malt to bakings with potato extract resulted in correlations equal to those obtained with other flour improvers.

Introduction

While the standard baking procedures in use at present require a certain amount of fermentable sugar as one of the chief ingredients, formulas which did not include this item have been used to some extent. Schnelle (12) employed a formula without sugar when studying different varieties of German wheat. He used a procedure including 4% yeast, 2% salt and water in proportion to the absorption of the flour. The fermentation temperature was 35°C., the dough being punched after 30 min. and the loaves panned after an additional 30 min. The proofing time was not rigidly fixed, and upon occasion varied as much as 30 min. or more. This method has been criticized by Jorgenson (8) on the grounds that no adequate distinction is made between the gassing power of the dough and the baking strength proper, due to the strong probability of yeast starvation resulting from lack of fermentable sugars necessary for the support of yeast activity during the fermentation period.

To date very little additional data have been published regarding the use of a baking formula without sugar, although various research workers have doubtless employed such a method at different times. It is quite probable, however, that some of the results obtained by this system of baking will be published in the near future.

As pointed out by Jorgenson, the principal weakness of a baking formula without fermentable sugar is the danger of yeast starvation in flours of low

diastatic activity, which, with the addition of sufficient sugar or malt to support yeast activity, would have produced satisfactory loaves. The lack of fermentable sugar confuses the issue, and would condemn a flour on the grounds of low diastatic activity and lack of baking strength. Further, commercial bakers almost universally use diastatic malt as well as sugar in some form in their formulas. A flour condemned in the baking laboratory because of failure to stand up without sugar could very possibly produce an excellent loaf when malt and sugar were added to supplement the available flour sugars.

Harris (5) published the results of a study on the baking qualities of a series of flours of various types with formulas which included different quantities of cooked potato. These formulas contained 2.5% of sugar in every case in addition to the potato material, and a marked improvement was noted in loaf volume and baking score for practically every flour examined. In view of the discussion concerning the omission of sugar, the author deemed it advisable to investigate further the use of cooked potato as applied to baking, especially with regard to its use in a formula without added fermentable sugar. Housewives are generally accustomed to the use of cooked potato in their home baking and would probably be interested in the production of equally satisfactory bread without the use of sugar. A further source of interest was the possibility of explaining part of the beneficial properties of the potato on the hypothesis that the carbohydrate from the potato serves as food for the yeast during the fermentation period.

TABLE I

DESCRIPTION AND CRUDE PROTEIN CONTENT OF FLOURS

No. of flour	Description	Crude protein, %
31	Soft winter wheat pastry	7.5
32	Unbleached middling's flour, 1930 and 1931 crops	10.7
33	First patent, blend of 1930 and 1931 crops	11.7
34	Baker's patent, milled from weathered 1931 crop	11.7
35	Baker's patent, milled from 1930 wheat	12.5
36	Second patent, from blend, 1930 and 1931	13.1
37	Unbleached straight, experimental 1° Reward	13.1
38	Baker's patent, from 1930 crop	13.5
39	Unbleached experimental straight No. 6 frosted	13.8
40	Unbleached break flour, blend 1930 and 1931	16.1
41	Strong first clear	17.6

A plan tentatively adopted was to bake a series of representative flours of varied baking strengths and characteristics, using formulas including (a) sugar, (b) no sugar, (c) potato and sugar, and (d) potato and no sugar.

Materials and Methods

The baking procedure was as follows: the doughs were mixed by hand in earthenware bowls and run in pairs at intervals of five minutes, the fermentation, proofing time and temperatures being those of the Blish (1) standard method. The following formula was used: flour, 100 gm.; yeast, 5 gm.; sugar, 2.5 gm.; salt, 2 gm.; distilled water as required for proper dough consistency.

This is called the simple formula No. 1 in this paper. The simple formula No. 2 is identical except for the omission of the sugar, while the potato treatments were obtained by adding to these two simple formulas 40 cc. of cooked potato extract at a suitable temperature. Potato extract rather than mashed cooked potato was used in the present instance because it was found to be more easily incorporated in the dough. In the subsequent bakings carried out with malt, potassium bromate, and cooked sweet potato, the two simple formulas were used in the same manner with the addition of the ingredients mentioned. The sweet potato was weighed directly into the 100 gm. of flour before mixing and the potassium bromate was introduced by means of a pipette, 2 cc. of the solution containing 0.002 gm. of the improver. The diastatic malt was weighed as accurately as possible and added to the flour before the other ingredients. Owing to the large quantities of other liquids necessary in some cases, it was more convenient to weigh the malt directly rather than to incorporate it as an aqueous solution.

A baking score was computed for these flours as follows:

Loaf volume	× 0.1	
Color of loaf	× 1.0	Maximum value 20
Grain of loaf	× 1.0	Maximum value 10
Texture of loaf	× 1.0	Maximum value 10

The sum of these individual scores was considered to be the baking value of the flour. Symmetry of the loaf was not scored, owing to its high correlation with loaf volume, and the tendency to cause very high total scores when used with strong protein flours.

The potato extract was prepared by boiling peeled and sliced white potatoes for approximately 35 min., the vessel being kept covered during the cooking process to avoid loss of moisture as much as possible. The thick liquid was then drained from the potato and allowed to stand and cool. After cooling to 20°C., the supernatant liquid was decanted from a white flocculent precipitate, and kept in an ice box until required. It was found to be impossible to keep the thick material in suspension when the liquid had cooled, with resulting variations in the concentration of potato. It appeared also, that a more uniform product was obtained by chilling and then draining off the liquid. This extract was kept not more than three or four days before using.

The sweet potato was prepared in a very similar manner, except that the water was allowed to evaporate during the cooking. The soft, moist slices were then thoroughly broken up and completely mixed by stirring. The potato, of a dark brown color, was partially dried and cooled to room temperature before using.

The series of flours used in this study was selected with a view to obtaining representative flours of the various types used in experimental baking.

Results

With simple formulas. In Table II are shown the loaf volumes and baking scores obtained with these flours when baked by the simple formulas. The

TABLE II

COMPARATIVE BAKING DATA OBTAINED WITH SIMPLE FORMULAS NO. 1 AND NO. 2

	Simple formula No. 1 (2½% sugar)					Simple formula No. 2 (no sugar)				
No.	Loaf volume, cc.	Color	Grain	Texture	Score	Loaf volume, cc.	Color	Grain	Texture	Score
31	330	12.0	4	2.0	51	290	10.0	4.5	1.0	44
32	550	12.0	9	8.5	84	515	13.0	9	8.5	82
33	520	20.5	9	9.0	90	530	19.5	5	5.0	82
34	515	17.0	6	6.0	80	560	19.0	3	4.0	82
35	514	16.5	8	7.5	83	530	16.0	7	7.0	83
36	540	16.5	8	8.0	86	560	17.0	6	6.0	85
37	540	15.0	8	7.0	84	465	16.0	7	6.0	65
38	525	16.0	6	7.0	81	380	15.0	3	3.0	59
39	545	11.5	7	7.0	80	475	11.0	5	6.0	69
40	570	12.0	7	7.0	83	460	11.5	7	6.0	70
41	540	8.0	4	3.0	69	570	6.0	2	1.0	66

loaf volumes exhibit no decided increase with increasing protein. In several samples, namely, Nos. 37, 38, 39 and 40, very decided decreases in loaf volume were evident when no sugar was used in the formula, as compared with the corresponding values obtained when sugar was included. This was probably due to starvation of the yeast, as pointed out by Jorgenson. No great differences in loaf color are displayed by the two systems of baking, but the grain and texture scores appear rather lower in the series baked without added sugar. With two exceptions, the latter series has a decidedly lower baking score as compared with the former. This is due primarily to lower volume, or lower grain and texture scores.

TABLE III

COMPARATIVE BAKING DATA OBTAINED BY ADDING 40 CC. OF POTATO EXTRACT TO SIMPLE FORMULAS NO. 1 AND NO. 2

	Simple formula No. 2 plus extract					Simple formula No. 1 plus extract				
No.	Loaf volume, cc.	Color	Grain	Texture	Score	Loaf volume, c.c.	Color	Grain	Texture	Score
31	260	10.0	4.0	2	42	290	10.5	4.0	2.0	45
32	620	13.5	9.5	8	93	610	14.0	8.0	7.0	90
33	560	22.0	8.5	9	95	630	22.5	9.0	9.5	104
34	750	21.0	4.0	5	105	692	21.5	5.0	4.0	99
35	550	16.0	6.5	7	84	628	17.5	7.0	6.5	94
36	600	18.0	7.5	8	93	650	19.0	7.0	8.5	99
37	405	14.0	5.0	5	64	560	15.5	4.0	4.0	79
38	340	13.0	3.0	2	52	550	16.0	6.0	7.0	84
39	405	10.5	5.0	5	61	645	13.0	5.5	6.5	89
40	435	10.0	3.0	4	60	680	12.0	6.0	6.0	92
41	530	7.0	2.0	1	63	640	6.5	2.5	2.0	75

With potato extract. In Table III are shown the loaf volumes and scores obtained by baking the flours with 40 cc. of potato extract added to the simple formulas and in Table IV those obtained with the addition of both 2% diastatic malt and potato to the No. 1 formula. The malt was used to increase the available supply of fermentable sugars when the yeast was stimulated by the potato material.

TABLE IV

BAKING DATA OBTAINED BY ADDING 40 CC. OF POTATO EXTRACT AND 2% DIASTATIC MALT TO SIMPLE FORMULA NO. 1

No.	Loaf volume, cc.	Color	Grain	Tex-ture	Score	No.	Loaf volume, cc.	Color	Grain	Tex-ture	Score
31	385	11.0	3.0	1.0	53	37	660	16.0	6.5	5.0	93
32	540	12.5	7.0	6.0	79	38	610	16.0	7.0	6.0	90
33	700	21.0	6.0	6.0	103	39	730	13.0	6.0	5.5	97
34	670	18.5	8.0	7.0	100	40	930	12.0	5.0	5.0	115
35	700	19.0	5.0	5.0	99	41	790	6.0	2.0	2.0	89
36	750	18.0	5.0	5.0	103						

The use of potato in addition to simple formulas Nos. 1 and 2 seems to accentuate the differences in loaf volume yielded by these formulas in the absence of potato. There appears to be a tendency toward higher color score when sugar is included in the potato bakings. These two factors, loaf volume and color score, tend to raise the baking score when sugar is used. The loaf color appears to fall off slightly when malt is used, due no doubt to the dark tinge contributed by this ingredient.

With sweet potato. Geddes and Winkler (4) found that honey and sucrose were equally valuable for the support of yeast fermentation in flour doughs. With their findings in mind and in view of the negative results obtained with cooked white potato, it was decided to try cooked sweet potato as a flour improver in a baking without added sugar. Flour No. 40, being exceedingly strong, and apparently lacking in diastatic power, was selected as a suitable sample to combine with various sweet potato treatments. The data obtained by combining this flour with increasing amounts of cooked sweet potato without other added fermentable sugars are shown in Table V. It would appear

TABLE V

THE EFFECT OF ADDING VARIOUS PERCENTAGES OF COOKED SWEET POTATO TO SIMPLE FORMULA NO. 2

Concentration of potato, %	Loaf volume, cc.	Color	Grain	Texture	Score	Remarks
0	460	11.5	7	6	70	Brown tinge im-
5	470	10.0	7	6	70	parted to the
10	520	9.0	5	5	71	loaf by the
20	690	8.0	3	3	83	potato
30	750	7.5	3	4	89	

from the data presented in this table that the sweet potato not only acts as a substitute for sugar but also has a decidedly stimulating effect upon the baking properties of the dough.   The color score is lowered, however, by the presence of the brown potato material.

To obviate this difficulty, an attempt was made to obtain an extract which would not have such a marked effect upon the color score.   Accordingly, extract No. 1 was prepared by boiling 180 gm. of sliced sweet potato in 360 cc. of water, the water being replenished to offset evaporation.   After 45 min. the liquid was drained from the still intact pieces of potato, and the process repeated on the residue with a fresh portion of water, obtaining a second extract, No. 2.   In this case, boiling was continued for only 20 min.   The extracts were then cooled and used separately with simple formula No. 2.

An addition of 40 cc. of extract No. 1 gave a loaf volume approximately equal to the corresponding value obtained with formula No. 1 alone.   The second extract was very weak in its effect, and reduced the loaf volume, probably due to a slight stimulation of the yeast without a corresponding increase in the supply of fermentable sugar.

A third extract, No. 3, was made by using 200 gm. of sweet potato and 200 cc. of water, employing the same procedure as before.   This extract

TABLE VI

THE EFFECT OF ADDING VARIOUS EXTRACTS OF SWEET POTATO TO SIMPLE FORMULA No. 2

Volume of extract added, cc.	Loaf volume, cc.	Color	Grain	Texture	Score
Extract No. 1. 180 gm. of sweet potato boiled for 45 min. in 360 cc. of water					
10	450				
20	490				
30	510				
40	560				
Extract No. 2. Made by boiling the residue from No. 1 for 20 min. in 360 cc. of water					
30	420				
40	410				
Extract No. 3. 200 gm. of sweet potato boiled for 45 min. in 200 cc. of water					
10	475	10.0	7	6	70
20	500	10.5	5	5	70
30	610	12.0	5	5	83
40	650	14.0	4	4	87
Extract No. 3 plus 2½% of sugar					
10	610	14.5	7	7	89
20	640	12.0	7	7	90
30	650	11.5	7	7	90
40	670	12.0	6	7	92

was used in portions of 10, 20, 30 and 40 cc., without sugar and with 2½%
of sugar. The loaf volumes and scores assigned the loaves made with these
extracts are shown in Table VI. The higher concentrations of this extract
increased the loaf color score over the values for the cooked sweet potato,
but the loaf volume was not as high as for the 30% mashed potato. The
baking score was very similar to that assigned to the loaves made with mashed
potato, but was increased when sugar was added to the formula.

In view of the larger loaves obtained with the sweet potato itself as compared
with the extract, as well as the large quantity of potato necessary to furnish
sufficient liquid to treat the entire series of flours, dried cooked sweet potato
was then used with all the flours in a concentration of 20%. The resulting
loaf volumes and baking scores are shown in Table VII.

TABLE VII

BAKING DATA OBTAINED BY ADDING 20% SWEET POTATO TO SIMPLE FORMULA
No. 2 (no sugar)

No.	Loaf volume, cc.	Color	Grain	Texture	Score	No.	Loaf volume, cc.	Color	Grain	Texture	Score
31	365	5.0	4.0	3.0	48	37	665	13.0	4.5	4.0	88
32	566	8.0	5.0	5.0	75	38	590	13.0	4.0	5.0	81
33	630	13.0	6.0	4.5	86	39	700	8.5	5.0	3.0	86
34	635	14.0	6.0	5.5	89	40	840	8.0	3.0	3.0	98
35	600	12.0	4.5	5.5	82	41	700	7.0	4.0	4.0	85
36	682	13.5	4.0	4.0	90						

An examination of this table shows that the loaf volumes tend to increase
with increasing flour protein. The color scores are all rather low, owing to
the darkening effect of the sweet potato, while grain and texture scores reflect
the "opening up" of the interior of the loaf through the action of the potato.
Those flours which, when baked without sugar gave poor loaf volumes as
compared with the values yielded with sugar, gave satisfactory results in
the presence of the sweet potato.

With potassium bromate and with potassium bromate plus malt. Two further
bakings were made with this series of flours, using 0.002% potassium bromate
with formula No. 2, and 0.002% potassium bromate plus 2% diastatic malt
with formula No. 1. Various workers in the field have used flour improvers,
including malt, with marked success in bringing out the full potentialities of a
flour. MacLeod (11), Larmour and MacLeod (10), and Larmour (9), in a
study of different series of Canadian wheat flours, found high correlations
between crude protein and loaf volume when potassium bromate, bromate and
malt, or Arkady and malt were included in the standard formula. Without
these flour improvers, the correlations were significantly lower. Harris (6, 7)
found also, in an investigation of the relations between total protein, protein
peptizability, and loaf volume, that these improvers raised the correlations
existing between the variables examined. Geddes (3), studying the effect
of heat treatment upon flour, concluded that potassium bromate in the baking

formula assisted in detecting injury to the flour quality, which injury, if the standard or basic formula alone had been used, would have escaped observation.

TABLE VIII

BAKING DATA OBTAINED WITH SIMPLE FORMULA NO. 2 PLUS 0.002% OF POTASSIUM BROMATE, AND WITH SIMPLE FORMULA NO. 1 PLUS 0.002% OF POTASSIUM BROMATE PLUS 2% OF DIASTATIC MALT

No.	Simple formula No. 2 plus 0.002% of potassium bromate					Simple formula No. 1 plus 0.002% potassium bromate plus 2% malt				
	Loaf volume, cc.	Color	Grain	Tex-ture	Score	Loaf volume, cc.	Color	Grain	Tex-ture	Score
31	295	16.5	3.0	1.0	50	355	12.0	2.0	2.0	51
32	530	17.0	7.0	8.0	85	488	13.0	8.0	7.0	67
33	570	21.0	5.0	7.0	90	540	15.0	6.0	6.0	81
34	580	16.0	8.0	6.0	88	580	15.0	5.0	4.5	82
35	540	19.0	4.5	6.0	83	560	14.0	6.5	6.0	82
36	620	19.0	7.5	8.0	96	620	14.0	6.0	7.0	89
37	600	19.5	6.0	5.0	90	580	15.0	5.0	5.0	83
38	470	18.0	8.0	7.0	80	580	12.0	5.0	6.0	81
39	690	16.0	7.0	5.0	97	680	13.5	3.0	3.0	87
40	705	13.0	7.5	7.0	98	870	15.5	3.5	3.5	109
41	675	9.0	4.0	4.5	85	820	9.0	4.0	4.0	99

In view of the utility of potassium bromate in evaluating flours, it seemed advisable to investigate the action of this bromate upon the flours used in the present study, and to compare the resulting data with those obtained by the methods already discussed. The baking results from the two series when treated with potassium bromate, with and without added sugar, are shown in Table VIII. Several of the flours showed a surprising increase in loaf volume when sugar and malt were included in the formula together with potassium bromate. The color score was decidedly lower when malt was present, this tendency being, in some instances, reflected in the baking score. The stronger flours, when sugar and malt were used, tended to give lower grain and texture scores as compared with the corresponding values obtained with bromate alone.

Comparisons of loaf volumes obtained with the various baking formulas. The loaf volumes obtained in all the bakings, together with the flour protein, are summarized in Table IX. Glancing first at the values yielded by the two simple formulas it is seen that No. 1 shows evidence of an increase in loaf volume, with increasing protein. This trend is not evident in the data yielded by method No. 2, where a sharp fall in volume occurs in samples Nos. 37, 38, 39 and 40. These flours appeared to be lacking in diastatic activity and consequently were unable to support properly yeast activity during the fermentation period. This fact is still more noticeable when the loaf volumes yielded after the addition of 40 cc. of potato extract are considered. Further decreases in loaf volume are evident with these particular flours when the above extract is used without the addition of fermentable sugar, but when sugar is added,

TABLE IX

COMPARATIVE LOAF VOLUMES (CC.) OBTAINED BY THE VARIOUS FORMULAS, ON A
BASIS OF 13.5% MOISTURE

No.	Protein, %	Simple formulas		Potato extract (40 cc.) plus simple formulas:			Sweet potato (20%) plus simple formula No. 2	KBrO₃ (0.002%) plus simple formulas:		Average loaf volume, cc.
		No. 1	No. 2	No. 1	No. 2	No. 1 + 2% malt		No. 2	No. 1 + malt (2%)	
31	7.5	330	290	290	260	385	365	295	355	321
32	10.7	550	515	610	620	540	566	530	488	552
33	11.7	520	530	630	560	700	630	570	540	585
34	11.7	515	540	692	750	670	635	580	580	620
35	12.5	514	530	628	550	700	600	540	560	578
36	13.1	540	560	650	600	750	682	620	620	628
37	13.1	540	465	560	405	660	665	600	580	559
38	13.5	525	380	525	340	610	590	470	580	502
39	13.8	545	475	645	405	730	700	690	680	609
40	16.1	570	460	680	435	930	840	705	870	686
41	17.6	540	570	640	530	790	700	675	820	658
Average		517	483	595	496	679	634	570	609	573

NOTE:—Simple formula No. 1 contains 3% yeast, 2% salt, 2½% sugar.
Simple formula No. 2 contains 3% yeast, 2% salt, no sugar.

large increases in loaf volume occur. These loaf volumes become still larger when diastatic malt, insuring a plentiful supply of fermentable sugar, is also present. The addition of potato in the absence of sugar gave loaf volumes in some cases appreciably greater than those obtained without potato but with sugar. In these samples a sufficient supply of fermentable sugar must either have existed from the beginning or must have been formed to meet the increased demands of the stimulated yeast fermentation. On the addition of both sugar and malt to the formula, not only did these flours show no further increase in loaf volume, but, in the cases of Nos. 32 and 34, there was a decrease. Flour No. 33 gave satisfactory results without added sugar, but produced a larger loaf when a supply of fermentable sugar was assured. The bakings with 40 cc. of potato extract plus sugar and malt generally yielded the largest loaves of the entire set of bakings represented in Table IX.

The treatments with 20% cooked sweet potato show increased loaf volumes in those flours which were unsuitable for use in a formula without sugar, and appear to give higher values than were yielded by the treatments with 40-cc. extracts of white potato plus 2½% sugar. When in addition diastatic malt was added, the use of extracts resulted in still greater volumes. These tendencies are reflected in the fact that the average loaf volumes are highest for the bakings with potato extract plus sugar and malt, and next highest for the sweet potato bakings. Sweet potato, in so far as loaf volume is concerned, is apparently able to supply any deficiency existing in a flour as well as, or better than, sucrose itself, but is not quite as satisfactory for this purpose as white potato, sucrose and diastatic malt.

The addition of .002% of potassium bromate resulted in greater loaf volume in both the presence and absence of 2½% of sugar, as is particularly exemplified by flours such as Nos. 37, 38, 39 and 40, the initial showing of which, owing to

the absence of sugar, was rather poor. Only two flours gave smaller loaf volumes when baked with potassium bromate and without sugar, than when baked with sugar and without potassium bromate. One of these flours was very weak, while the other, No. 38, acted throughout as if it were lacking in the ability to produce any appreciable amount of fermentable sugar.

When 2% of diastatic malt was added in addition to the potassium bromate, an appreciable increase in loaf volume resulted in the cases of higher protein flours. The averages obtained with bromate plus malt are the third highest in the table. The final average loaf volumes for all the bakings show the effect of the low diastatic flours which, yielding very low volumes for some of the bakings, lower the average results.

Upon examination of the data presented in Table IX with respect to the behavior of individual flours under the various treatments, it appears that No. 34, which was commercially milled from wheat which had been exposed to several rains interspersed with drying weather, gave exceptionally satisfactory results without the addition of any form of sugar. This tendency can probably be explained on the grounds of increased diastatic activity due to exposure to moisture and warm weather while in the stook. Sample No. 40 was quite different in its response to the various baking formulas. Though an exceedingly strong flour, it was unable to produce large loaves without added sugar, there being a difference of 495 cc. between the minimum and maximum loaf volumes. The two experimental flours, Nos. 37 and 39, exhibit the same tendency in lesser degree. Potassium bromate appears to function in the cases of these flours in much the same manner as a formula containing sugar in addition to a flour improver. No. 39 showed no trace of having suffered injury through frost damage. The clear flour, No. 41, did not, with any of the treatments, produce as large a loaf as did No. 40, although it contained more protein than the latter.

Discussion of correlation coefficients. The correlation coefficients computed between flour protein and loaf volume are given in Table X. The significance

TABLE X

CORRELATION COEFFICIENTS COMPUTED BETWEEN FLOUR PROTEIN AND LOAF VOLUME

Baking formula	Correlation coefficient
Simple No. 1	+.734
Simple No. 2	+.494
Simple No. 1 plus 40 cc. potato extract	+.620
Simple No. 2 plus 40 cc. potato extract	+.104
Simple No. 1 plus 40 cc. potato extract plus 2% malt	+.866
Simple No. 2 plus 20% sweet potato	+.856
Simple No. 2 plus 0.002% potassium bromate	+.838
Simple No. 1 plus 0.002% potassium bromate plus 2% malt	+.954
Average loaf volume, by all formulas	+.804
Value of r at 5% point	+.602
Value of r at 1% point	+.708

NOTE:—Formula No. 1 contained 3% yeast, 2% salt, 2½% sugar.
Formula No. 2 contained 3% yeast, 2% salt, but no sugar.

of these coefficients may be judged by comparison with the points of minimum significance according to the number of pairs of observations. These values have been tabulated by Fisher (2). The coefficients are calculated from 11 pairs of values and the 5% and 1% points are respectively .602 and .708.

The coefficients obtained by the use of the baking methods without added fermentable sugar are not significant, and show the importance of this ingredient in baking a series of flours of the types used in this study. When potato extract was used, the inclusion of sugar in the formula raised the correlation coefficient to a value between the 5% and 1% points. When diastatic malt was also added, the coefficient becomes significant for the 1% point.

In order to determine whether the differences between any of the constants were significant, the Z test proposed by Fisher (2, p. 170) was used. This test depends upon the substitution of a value, Z, for each value of the correlation constant r.

The significance of the difference between any two correlations may be expressed by the ratio of the difference in Z values $(Z_1 - Z_2)$ to the standard error $\sqrt{\dfrac{1}{n_1 - 3} + \dfrac{1}{n_2 - 3}}$. If this ratio is 2 or greater the difference is significant.

The standard error may be calculated from the square root of the sum of the reciprocals of the number of samples in each correlation, minus 3. In the present case, where the number of samples is 11, $n - 3 = 8$ and the expression for the standard error of Z becomes $\sqrt{\frac{1}{8} + \frac{1}{8}} = .500$. Substituting the values from Table X, we find, Table XI, that there is a significant difference between the correlation constants obtained with the use of bromate and malt, and the value yielded by formula No. 1 plus 40 cc. of potato extract. The difference between the constants for the malt-bromate method and simple formula No. 1 is not significant, while in the presence of sugar and white potato, the difference occasioned by the introduction of diastatic malt is still further removed from significance. Apparently, with the exception of the formulas without sucrose, and without malt but with potato, approx-

TABLE XI

TEST OF SIGNIFICANCE OF DIFFERENCE BETWEEN THE COEFFICIENTS

r	Z	$Z_1 - Z_2$	$\sqrt{\dfrac{1}{n_1 - 3} + \dfrac{1}{n_2 - 3}}$	$\dfrac{Z_1 - Z_2}{\sqrt{\dfrac{1}{n_1 - 3} + \dfrac{1}{n_2 - 3}}}$
.954 .620	1.874 .725	1.149	.500	2.298
.954 .734	1.874 .937	.937	.500	1.874
.866 .620	1.317 .725	.592	.500	1.184
.734 .494	.937 .541	.396	.500	.792

imately equal correlations between loaf volume and protein content are obtained by all baking methods.

The conclusions reached in the present study regarding the effect of cooked white potato extract are similar to the results obtained by the author in a previous investigation in which dried mashed potato was added to a series of flours. In the presence of sucrose, the addition of potato improved both color and volume, while loaf volume and flour protein were found to be highly correlated.

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SNOWFALL IN MONTREAL[1]

By R. De L. French[2]

Abstract

This paper presents a study of the snowfall records of Montreal from 1875 to 1931. The conclusion is reached that the decrease in recorded snowfall is probably due to increase in the city's heat radiation, of which a rough estimate is offered.

A method for predicting future seasonal snowfalls is suggested. The distribution of snowfall by months and by storms is investigated, and data concerning the length of the snowy season and the intensity of snowfalls are presented.

Snow interferes with transportation, and embarrasses the contractor who must operate in the winter. The growth of motor travel has made it necessary for cities to clear their streets and it is probable that before many years all main highways will have to be kept passable for motor vehicles throughout the winter. Construction operations are no longer halted by low temperatures, but are and always will be hindered by snow.

Methods of removing and disposing of snow are well developed and fairly satisfactory, though progress is constant. The essence of all these methods is organization, so that the system can be put in operation at short notice when snow begins to fall, and continue to function smoothly so long as the necessity exists. However, there appears to be no way in which this highly perfected, and, generally speaking, efficient organization can determine in advance the approximate scope of its labors. There is no hope that the date, duration and magnitude of every snow storm to come can be predicted, but the possibility that a study of records of past snowfalls might yield useful data certainly exists.

An attempt has been made herein to find rational answers to questions such as these:

(a) Can the total snowfall in any future winter be foretold accurately enough so that the prediction may be of value?

(b) Which months have heavy snowfalls, which light, and how great are these falls?

(c) How often do storms of various durations occur?

(d) What is the usual length of the snowy season, when does it begin and when end?

(e) On how many days in each month during the winter may snow be expected to fall?

(f) What are the frequencies of various rates of snowfall lasting one day, lasting two days, etc.?

(g) How much snow may be expected to fall in one day, in two days, etc.?

Records Used

The records considered are those taken at the McGill University Observatory. Previous to 1875 meteorological observations were not regularly made in Montreal, and few of the early data survive.

Measurements of heavy snowfall, say six inches or over, are made on the western half of the University campus, a substantially level field of between four and five acres. Although this field is partly surrounded by trees and buildings, these are so low that they cannot have any very marked sheltering effect on the central part of the area, where depth measurements are made. Light snowfalls are measured adjacent to the Observatory building. The choice of the observing point is governed largely by conditions during the storm, every effort being made to assure the representative character of the measurements.

Total Snowfall

Total snowfall is reported by the meteorological service in inches per calendar year; each annual record includes parts of two winters. Such disjointed records obviously do not present as accurate a picture of actual conditions as do records for each winter as a unit, *i.e.*, for the period commencing in October of one year and ending in April of the following year. The records of snowfall on which the studies of this paper are based were therefore rearranged in this way. Only storms during which at least 0.1 inch of snow fell are included, this being the usual meteorological fraction.

In Fig. 1, upper curve, the total snowfalls for each winter from 1875-76 to 1930-31 are plotted from the data in Table I. Although there is a wide variation in snowfall from winter to winter, the graph suggests that there is a distinct downward trend throughout the period covered. This is noticeable in the graph of the 10-year moving average, and is most clearly shown by the line marked "Trend." The wavy character of the moving average line also suggests a periodicity in seasonal snowfalls to which reference will be made later. The "Trend" line is located according to the method of least squares, that is, so that the sum of the squares of the deviations of the various points from it is reduced to the minimum, and therefore it is the most probable straight line which can be drawn through this group of points.

The downward slope of the trend indicates that the seasonal snowfall recorded in Montreal has been decreasing since 1875-76, or, if there has been a lesser downward slope during the past few years, this change has not yet become sufficiently pronounced to overcome the downward trend of the records in the earlier years. The reasons for this apparent decrease in snowfall are largely a matter of opinion, but it will be useful to speculate a little about them.

Perhaps the records of later seasons do not represent the true snowfall, or perhaps there has been a real decrease in recorded snowfall. Faulty records may be due to the fact that the reporting station has been unfavorably influenced by the erection of buildings and the like. The Montreal station has probably been so influenced, but it is difficult indeed to believe that the average decrease in snowfall of about one-half inch per season can be caused entirely by such factors.

A much more likely explanation is that, as the density of population around the station increases with the growth of the city, more and more heat is radiated to the atmosphere, tending to melt or even to evaporate some of the snow
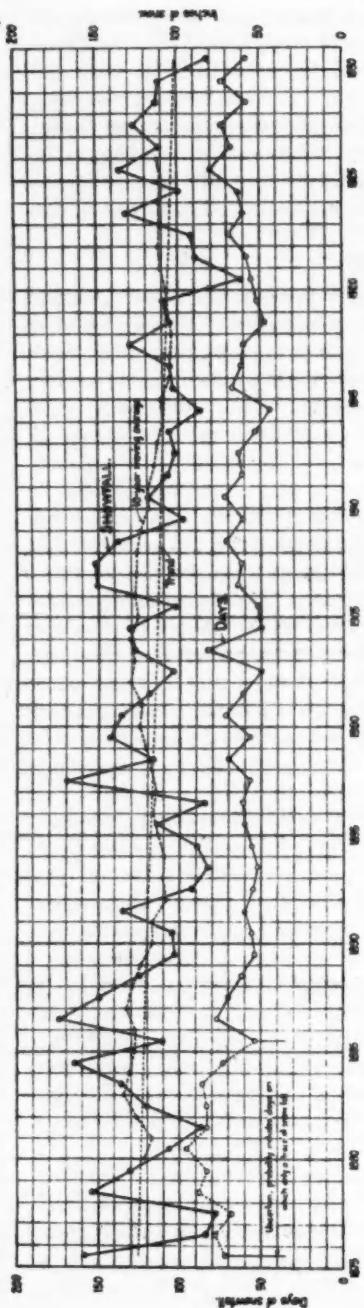
FIG. 1. Montreal snowfall by winters.
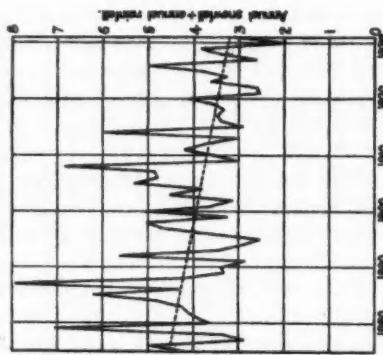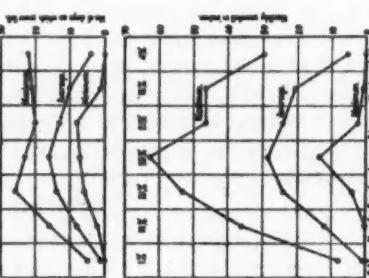
FIG. 4. Monthly distribution of snowfall and days of snow per month in Montreal.
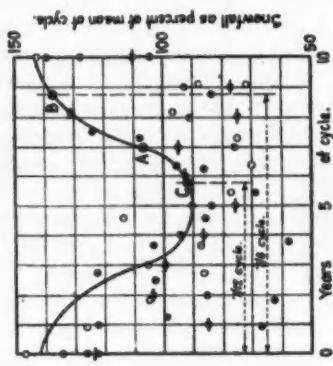
FIG. 3. Cyclic variation of seasonal snowfall in Montreal.

FIG. 2. Ratios of annual snowfall to annual rainfall in Montreal.

TABLE I

SNOWFALL IN MONTREAL
SUMMARY OF MONTHLY SNOWFALL, 1875-1931

Winter	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	Total
1875–76	0.0"	21.7"	24.2"	27.4"	22.5"	45.6"	12.0"	158.7"
1876–77	1.0	0.1	23.6	23.3	3.6	22.4	10.2	84.2
1877–78	5.4	5.1	4.3	30.5	10.2	19.4	2.3	78.2
1878–79	0.1	14.6	32.8	39.5	27.4	32.6	6.9	153.9
1879–80	0.0	16.8	37.4	16.3	26.0	25.1	8.6	130.2
1880–81	3.1	12.7	17.6	26.5	7.3	39.1	0.4	107.9
1881–82	0.1	11.8	4.4	28.2	23.2	15.3	3.2	86.7
1882–83	0.0	1.0	39.8	20.0	17.2	35.5	6.7	120.2
1883–84	0.0	12.1	25.5	44.2	29.3	20.9	3.9	135.9
1884–85	0.5	5.0	35.0	21.5	43.5	29.1	29.8	164.4
1885–86	2.8	14.4	36.5	17.4	10.3	26.5	2.8	110.7
1886–87	0.5	36.1	22.4	50.1	34.1	31.1	0.0	174.3
1887–88	3.1	25.9	24.9	33.6	30.0	25.2	7.1	149.8
1888–89	7.8	11.0	17.6	40.5	32.2	15.3	0.1	124.6
1889–90	0.8	15.6	13.2	31.3	27.4	11.7	3.0	103.0
1890–91	1.5	8.8	32.3	21.0	18.7	16.3	7.1	104.2
1891–92	1.5	3.5	12.0	39.7	36.4	34.6	7.2	134.9
1892–93	0.0	22.1	12.3	22.4	21.1	6.1	8.4	92.4
1893–94	0.0	5.8	40.4	19.2	9.1	7.4	1.2	83.1
1894–95	0.0	11.0	23.0	24.9	24.7	5.6	0.9	89.2
1895–96	0.8	12.7	12.0	20.7	25.9	39.5	3.2	114.8
1896–97	0.0	5.9	10.8	26.1	16.5	23.7	1.9	84.9
1897–98	0.0	18.9	39.2	62.7	46.3	0.9	0.7	169.7
1898–99	0.0	15.7	20.9	25.1	9.1	43.7	1.9	116.4
1899–1900	0.0	2.4	24.9	36.6	31.5	46.4	0.7	142.5
1900–01	0.0	34.8	25.2	27.1	22.4	26.0	1.3	136.8
1901–02	1.0	29.2	15.1	26.6	34.5	9.4	3.4	119.2
1902–03	0.0	5.9	31.3	33.5	26.2	3.1	4.3	104.3
1903–04	1.5"	5.4"	38.7"	38.3"	21.5"	15.9"	6.5"	127.8"
1904–05	1.0	10.6	30.3	45.6	38.9	2.7	2.5	130.6
1905–06	1.0	13.3	28.7	15.2	18.4	18.3	8.2	103.1
1906–07	0.5	22.4	40.5	22.8	26.7	19.8	17.8	150.5
1907–08	0.0	14.2	31.2	44.5	40.6	12.2	9.2	151.9
1908–09	0.0	13.3	53.2	22.1	20.3	20.9	8.9	138.8
1909–10	0.5	9.4	13.2	30.5	37.8	5.1	1.2	97.2
1910–11	1.5	8.9	24.9	17.0	31.6	32.8	4.2	119.9
1911–12	0.0	8.9	12.8	30.6	36.7	14.8	2.2	107.5
1912–13	0.1	22.1	14.1	22.5	22.4	19.0	2.3	102.5
1913–14	0.1	4.7	27.5	31.2	14.9	23.0	4.5	105.9
1914–15	0.6	20.3	25.9	15.6	17.7	4.6	0.0	86.6
1915–16	0.2	2.0	19.4	17.7	28.1	22.8	6.7	103.2
1916–17	0.2	3.4	20.9	40.2	21.1	19.0	2.0	105.3
1917–18	0.0	12.0	18.5	34.0	34.5	26.1	2.1	129.6
1918–19	0.0	3.3	11.4	16.8	18.6	43.2	4.4	104.8
1919–20	0.2	10.7	21.4	29.4	29.3	27.9	0.7	109.2
1920–21	0.2	10.9	4.3	13.6	9.1	0.9	0.3	61.6
1921–22	3.5	20.6	13.5	20.6	19.4	6.9	8.2	89.3
1922–23	0.0	1.9	15.1	23.5	23.6	24.4	17.1	92.0
1923–24	0.0	15.0	23.6	35.5	26.4	14.0	7.6	131.6
1924–25	3.2	5.3	16.4	41.2	12.2	16.9	11.7	99.6
1925–26	0.0	10.1	25.2	18.2	31.1	36.0	0.3	135.5
1926–27	0.6	15.1	35.4	19.4	34.7	5.8	11.8	111.3
1927–28	0.0	6.9	34.4	37.3	14.1	23.0	11.0	127.5
1928–29	0.0	11.8	13.0	29.4	21.5	16.2	11.0	102.9
1929–30	0.3	3.8	41.4	28.8	11.4	12.3	3.3	101.3
1930–31	0.0	5.4	12.5	31.8	23.7	8.3	0.0	81.7
Maximum	7.8	36.1	53.2	62.7	46.3	46.4	29.8	174.3
Minimum	0.0	0.1	4.3	13.6	3.6	0.9	0.0	61.6
Mean	0.8	12.0	24.1	28.7	24.3	20.6	5.3	115.8

when it reaches a zone not far above the earth. Such heat radiation also increases the capacity of the air to absorb moisture, but presumably has little or no effect on winds tending to dissipate the heat. Since most snow falls when temperatures are close to 32° F., a rise of a degree or two in atmospheric temperature may determine the nature of the precipitation, whether snow or rain.

Total precipitation as measured at Montreal has been reasonably uniform over the period for which records are available. Wet and dry years offset one another so that the general trend of the records shows little tendency toward either increase or decrease. If total precipitation remains nearly constant, then decrease of snowfall should be accompanied by increase of rainfall, and a decrease in the ratio of annual snowfall to annual rainfall would indicate both a decrease in snowfall and an increase in rainfall. This argument holds rigidly only if a unit depth of snow is equivalent to a constant depth of rain. This is not strictly true, but since one winter's snowfall is the sum of many small falls of all kinds of snow, wet and dry, the mean rainfall equivalent of unit snowfall varies little from season to season.

In Fig. 2 the ratios of annual snowfall to annual rainfall in Montreal for the past 57 years have been plotted. It is quite apparent that these ratios are decreasing; the trend of the decrease being shown by the straight line, which has been located by the methods of least squares.

These facts all lead to the conclusion that the explanation of Montreal's decreasing recorded snowfall lies in the increasing melting of aerial snow by heat radiated from the city. This conclusion is fortified by the fact that snowfall records from areas where natural conditions obtain do not show any such consistent decrease.

It is quite impossible to make any really valuable estimate of the heat radiation of a city; it is thought that in this latitude and type of climate it may easily reach 10,000 B.t.u. per person per hour during cold weather, which is equivalent to 500,000 B.t.u. per hour per acre with the rather moderate population density of only 50 persons per acre.

Short-time Cycles

In addition to the probable long-time cycles of variation in seasonal snowfall, shorter cycles are apparent from the graph of Fig. 1, and are shown in Table II. For the sake of comparison, records from Ottawa and from Quebec are also included in this table.

The lengths of the cycles agree fairly well. There is no marked peak in the Ottawa records between 1887 and 1908, and none in the Quebec records between 1882 and 1908, periods of 21 and 26 years, respectively. The fact that these records are for calendar years and not for winters may mask the peaks in some degree; this effect is noticeable in the Montreal records. The mean length of this short-time cycle appears to lie between 10 and 11 years, which agrees roughly with the sunspot cycle of 11.2 years, with which other meteorological phenomena are frequently correlated, but one should not give this coincidence much emphasis.

TABLE II

SHORT-TIME SNOWFALL CYCLES IN MONTREAL, OTTAWA AND QUEBEC

Montreal		Ottawa		Quebec	
Winter	Years, peak to peak	Year	Years, peak to peak	Year	Years, peak to peak
1875–76		1876		1874	
	11		11		8
1886–87		1887		1882	
	11		11		
1897–98		1898?		??	26
	10		10		
1907–08		1908		1908	
	10		9		9
1917–18		1917		1917	
	8		9		11
1925–26		1926		1928	
Mean	10		10		11

In Fig. 3 is given a further analysis of each of the five cycles into which the records of seasonal snowfall in Montreal have been divided. Ten years has been adopted as the length of the basic cycle; ordinates have been evenly interpolated between 0 and 10 for cycles differing in length from 10 years. The curve in the figure is located so that when it is used in predicting future snowfalls, the results are more likely to be in excess of the truth than deficient, *i.e.*, so that the predictions are on the safe side.

Prediction of Probable Future Seasonal Snowfalls

Predictions of future seasonal snowfalls based on the foregoing data cannot be less accurate than the blind guesses which must otherwise be made.

To illustrate the method of prediction suggested, assume that the probable snowfall for the winter of 1932-33 is desired. This is seven years after the beginning of the 1925-26 cycle. The mean decrease in seasonal snowfall during a ten-year cycle is about 4.5 in., as read from the "Trend" line of Fig. 1. The mean seasonal snowfall for the cycle beginning in 1917-18 and ending in 1925-26, as computed from Table I, is 105.9 in. Therefore the probable mean seasonal snowfall for the cycle including the winter of 1932-33 is $105.9 - 4.5 = 101.4$ in. From Fig. 3, Point A, the seasonal snowfall in the seventh year of a 10-year cycle may be expected to be not more than 106% of the mean for the cycle. Then the probable maximum value for the snowfall during the winter of 1932-33 is $101.4 \times 1.06 = 107.5$ in.

The length of the cycle beginning in 1925-26 is unknown, but was assumed to be 10 years. If it were assumed at eight years, the prediction just made would be increased in the ratio of 1.37 to 1.06 (Fig. 3, Point B), or by about 29% to 139.0 in. On the other hand, if 12 years were assumed as the length of the cycle, the prediction would be reduced to the ratio of 0.92 to 1.06 (Fig. 3, Point C), or by about 13% to 93.5 in. The probability of the length of a cycle varying this much is not great, if past records are criteria.

If snowfall predictions for 1887-1931 are made from the 1875-1887 cycle by the method just outlined, the errors shown in Table III result.

TABLE III

SUMMARY OF ERRORS IN SNOWFALL
PREDICTIONS, 1886–87 TO 1930–31

Sign	No. of errors	Per cent error		
		Maximum	Minimum	Mean
−	14	19.5	0.8	6.4
+	35	96.0	0.8	24.3
+ and −	49	—	—	15.5

Standard deviation = 3.9

Thirty-two of the 49 predictions are within 20% of the true value; this is thought to be a reasonable limit for work of this kind. Although this is by no means a conclusive test of the accuracy of the method, it does serve to show that it offers possibilities of usefulness.

Monthly Distribution of Snowfall

TABLE IV

EARLY AND LATE SNOW-
FALLS IN MONTREAL

Date	Snowfall, in.
Sept. 1912	0.1
Sept. 1913	0.1
May 1876	0.3
May 1878	1.0
May 1882	0.5
May 1889	0.1
May 1909	0.1

The distribution of snowfall month by month is shown in Table I; at the foot of the table maximum, minimum and mean values are given. These data are also presented in graphical form in Fig. 4. The figures across the top of the lower part of the chart give approximate mean percentages of the total seasonal snowfall occurring in each month.

Records for September and for May have been omitted from this chart as well as from Table I because there are only occasional snowfalls in these months. Since regular observations have been made in Montreal, early snowfalls and late ones have been reported as shown in Table IV.

Distribution and Frequency of Storms of Various Durations

For the purposes of this paper, a storm is considered to mean a single day, or two or more consecutive days, during which 0.1 inch or more of snow fell. Thus, a storm may include several periods of snowfall, separated by intervals of no snowfall, roughly corresponding to the passage of an anticyclonic depression in that succession of highs and lows that dominate our weather.

One-tenth inch of snow may be regarded as too small a fall to be of any consequence, but it should not be forgotten that it is impossible to foretell the probable fall when a storm begins, and that the essence of successful snow fighting is to set the organization functioning promptly at the onset of a storm.

Table V shows the number of days of snowfall in each month since the beginning of the Montreal records; the lower curve of Fig. 1 gives the same information in graphical form. The maximum, minimum and mean number of days of snow for each month are given at the foot of the table, and these data are shown graphically by the curves at the top of Fig. 4.

TABLE V
SNOWFALL IN MONTREAL
NUMBER OF DAYS IN EACH MONTH ON WHICH 0.1 IN. OR MORE OF SNOW FELL

Winter	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	Total
1875–76	1	16	—	16	15	17	7	72
1876–77	2	5	19	21	11	16	4	78
1877–78	2	8	12	18	12	14	2	68
1878–79	2	12	24	23	16	16	5	88
1879–80	1	8	21	11	16	16	10	83
1880–81	5	15	18	18	11	21	8	96
1881–82	5	13	12	20	13	15	5	83
1882–83	0	5	24	16	16	15	7	83
1883–84	0	8	17	21	20	14	6	85
1884–85	5	10	14	12	11	12	9	73
1885–86	1	7	14	17	11	1	3	54
1886–87	1	15	13	19	15	14	0	77
1887–88	3	13	10	13	14	9	8	70
1888–89	4	6	12	14	15	10	1	62
1889–90	1	4	13	16	11	7	2	54
1890–91	0	6	16	12	14	6	2	56
1891–92	2	5	6	21	13	9	4	60
1892–93	0	11	12	12	9	7	1	55
1893–94	0	6	18	13	9	5	4	52
1894–95	1	11	10	14	12	9	5	56
1895–96	0	5	8	13	16	12	6	60
1896–97	1	7	9	14	10	10	4	61
1897–98	0	5	16	18	13	1	11	57
1898–99	0	6	19	17	11	15	4	70
1899–1900	0	2	11	14	12	15	3	57
1900–01	0	12	17	13	11	18	1	72
1901–02	1	14	11	14	13	6	2	61
1902–03	0	3	16	14	10	4	3	50

Winter	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	Total
1903–04	1	14	22	18	15	10	3	83
1904–05	0	4	13	14	13	2	4	50
1905–06	1	5	16	10	9	8	3	52
1906–07	1	9	11	15	18	8	2	64
1907–08	0	7	12	18	11	8	6	62
1908–09	0	6	22	17	11	11	4	71
1909–10	1	7	15	15	17	6	1	61
1910–11	2	7	18	17	12	14	3	72
1911–12	0	9	7	18	13	8	4	61
1912–13	1	10	12	14	16	9	2	63
1913–14	0	2	9	15	9	12	5	53
1914–15	1	8	9	7	7	7	0	44
1915–16	2	5	13	14	11	10	6	67
1916–17	0	5	11	18	19	12	2	62
1917–18	1	9	7	17	13	10	2	60
1918–19	0	3	10	14	9	7	4	47
1919–20	0	6	9	14	13	8	2	52
1920–21	1	12	14	11	12	4	1	55
1921–22	1	13	9	14	12	5	4	58
1922–23	2	4	13	13	13	18	6	69
1923–24	0	5	9	18	10	12	6	60
1924–25	0	5	15	22	10	7	4	63
1925–26	5	2	15	17	14	15	12	80
1926–27	2	12	19	15	15	3	1	67
1927–28	0	8	11	17	17	13	7	73
1928–29	1	5	8	17	13	8	7	58
1929–30	1	8	26	14	8	13	3	73
1930–31	0	4	12	13	19	10	0	58
Maximum	5	16	26	23	20	21	12	96
Minimum	0	2	6	7	8	1	0	44
Mean	1	8	14	16	13	10	4	65

A tabulation of the distribution of storms of different durations is given in Table VI.

TABLE VI

MONTHLY DISTRIBUTION OF SNOWSTORMS OF VARIOUS DURATIONS IN MONTREAL

Month	Duration of storm in days										
	1	2	3	4	5	6	7	8	9	10	11
Oct.	28	4									
Nov.	90	42	24	9	3	3	1	1			
Dec.	134	84	22	17	14	4	2	1	1		1
Jan.	136	101	36	21	13	3	5			1	1
Feb.	118	92	30	18	8	5	2	2	2		
Mar.	108	64	30	10	5	3	1	1			
Apr.	77	17	8	5							
Total storms	691	404	150	80	43	18	11	5	3	1	2
Total days	691	808	450	320	215	108	77	40	27	10	22
% of total days	25	29	16	12	8	4	3	1	1	0	1
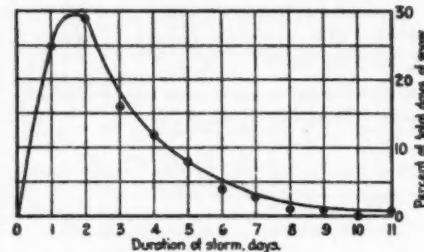
FIG. 5. *Frequency of snow storms of various durations in Montreal.*

A clearer idea of the frequency of storms of various durations is given by Fig. 5, which has been plotted from the data of this table. It will be noted that only about 11% of the total number of days of snow occurs in storms lasting more than five days.

Length of Season of Snowfall

The earliest date of snowfall, excluding those given in Table IV, was October 3; the mean date of the beginning of the snowy season is October 30. Excluding the dates given in Table IV, the latest snow fell on April 30, while winter usually ends about April 17. The interval between the first snowfall and the last of the season varied from 137 to 224 days, with a mean length of 170 days. Table V shows that snow fell on from 44 to 96 days; during an average winter there were about 65 days of snowfall. This is equivalent to saying that snow falls to the amount of at least 0.1 in. on four days out of ten from November 1 to April 15.

Intensity of Snowfalls

A series of curves has been plotted in Fig. 6 from the analysis of 2,862 single days of snowfall, and from records of 1,837 days comprising storms up to and including five days' duration. The records of the shorter storms are not included in those of the longer, except in the case of single-day storms, which are so included.

FIG. 6. *Frequency of various storm snowfalls in Montreal.*

TABLE VII

SIX- TO ELEVEN-DAY STORMS IN MONTREAL

Duration, days	Number of records	Snowfall, in.	
		Minimum	Maximum
6	17	4.5	17.4
7	13	1.8	23.5
8	5	8.0	21.3
9	2	15.2	26.0
10	2	14.5	24.6
11	2	13.5	29.4

The points plotted are those which rough-ly define the envelopes of the groups: other points have been omitted for the sake of clearness. The curves therefore give values which have been exceeded only rarely in the past, and which are equally unlikely to be exceeded in future.

From these graphs, the maximum and the minimum snowfall of record, and the limiting probability of the occurrence of any snowfall between them for any of the storms represented may be determined. The curve for the four-day storms, for example, shows that the falls have ranged between 0.9 and 23.1 in.; a fall of 18 in. occurs in not more than 2% of such storms.

Records relating to storms lasting longer than five days are not numerous enough to be included in Fig. 6. Table VII gives some data regarding such storms. There are no records of storms lasting longer than 11 days.
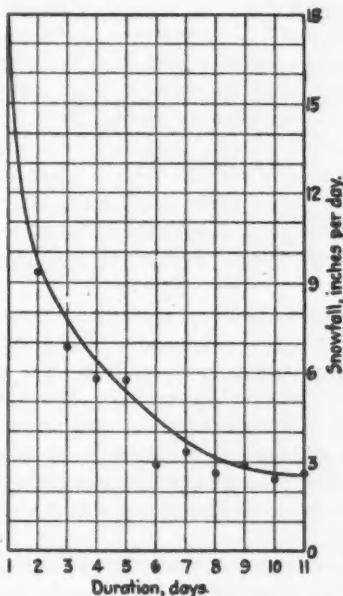
FIG. 7. *Maximum daily snowfalls for storms of various durations in Montreal.*

Maximum daily rates of snowfall for storms of different durations are shown in Fig. 7.

Acknowledgments

ON TWO NEPHELINE-SODALITE-SYENITES FROM NEW LOCALITIES IN NORTHERN RHODESIA[1]

By Frank Dawson Adams[2] and Freleigh Fitz Osborne[3]

Abstract

Two specimens of nepheline-sodalite-syenite from Northern Rhodesia are petrologically interesting because of the low content of binary oxides and the presence of an aluminous aegirine. The rocks are similar in chemical composition to lavas found at the north end of Lake Nyassa and probably belong to the same petrographical province.

Introduction

In a recent communication Dr. J. Austen Bancroft, Consulting Geologist of the British South Africa Company, writing from Nkana, refers to a number of discoveries of great scientific interest that are being brought to light through the detailed geological survey of the Company's concession in Northern Rhodesia, which is being actively prosecuted by a large staff of geologists under his direction. These will be described in detail when the work has been completed. Among the newly discovered occurrences, which promise to be of special interest to petrographers, are large areas of alkaline rocks. During the months of November and December of last year two widely separated areas of these were found. The rocks constituting these occurrences, Dr. Bancroft states, are very similar in appearance to the nepheline-bearing rocks, described by Adams and Barlow, in the Haliburton District of Ontario, some of them being rich in sodalite, cancrinite, etc.

The writers have received from Dr. Bancroft two of the first specimens of these rocks which have been collected. This paper presents the results of a petrographical examination of them, which must of course be supplemented by a detailed study of the whole petrographical province as the survey is continued. It serves merely to set forth in some detail the character of these two specimens of Rhodesian nepheline syenites, to show that they are rocks of peculiar interest, and to indicate that a further study of the area from which they are derived will probably bring to light a highly interesting series of co-magmatic rocks.

The specimens received from Dr. Bancroft were labelled *A* and *B*, respectively. *A* is a nepheline-sodalite-syenite from a point 40 miles west of Solwezi, and a short distance south of the boundary line between Northern Rhodesia and the Belgian Congo. Solwezi is 80 miles in a westerly direction from Elizabethville.

B is a nepheline-sodalite-cancrinite-syenite from the northeast corner of Northern Rhodesia at a point between the Loangwa River and the border of Nyassaland. It is about 65 miles south of Fort Hill. The two localities are about 500 miles apart.

Nothing is known by the writers concerning the age or geological relations of these igneous rocks. In Fairweather's geological map of Northern Rhodesia, which is reproduced in Krenkel's *Geologie Afrikas* (1, p. 488), the locality from which specimen *A* was taken is indicated as Muschinga schist and Lumagundi schists (Broken Hill schists) in intimate association, while the locality from which specimen *B* was taken is shown as Karru beds but not very far distant from a large occurrence of gneisses and ancient crystalline schists.

Both specimens were evidently taken from outcrops and each shows one weathered surface. While this may be termed a weathered surface, the rocks as a matter of fact show no alteration from the action of the weather. They are perfectly fresh and show no decomposition products, but the surface which has been exposed to the weather resembles that displayed by the nepheline syenites of the Haliburton District in Ontario in that the feldspathic constituents stand out from it in relief, whereas the nepheline, sodalite and other feldspathoids occupy depressed areas as if these minerals had been dissolved away by the action of the weather.

Thirty-two thin sections of the rocks were prepared and examined.

Specimen A.   Nepheline-sodalite-syenite (Aegirine-ditroite)

Forty miles west of Solwezi and south of the boundary between Northern
    Rhodesia and the Belgian Congo

The rock is of medium granularity with four constituents visible on the fresh surface.   White feldspar, which shows Carlsbad twinning and a tendency to form radiating groups, is the most abundant constituent.   Pale-blue sodalite forms patches interstitial to the feldspar.   Nepheline, of a paler blue than the sodalite, forms cores to some areas of sodalite.   A pale-green pyroxene is present in fibrous clots.   The feldspar is the only constituent showing any tendency toward idiomorphism.   This is especially evident on the weathered surface, where the feldspathoids have been removed, and the feldspar laths form a boxwork around the depressions.

Fifteen thin sections of the rock were examined.   They show microcline, albite, aluminous aegirine, nepheline, and sodalite, as the principal constituents. Zircon, calcite, magnetite, hematite, cancrinite, perovskite, a hydrated iron oxide, and an unidentified mineral are accessory.

A determination of the proportions of minerals by the Rosiwal method reduced to weight per cent gives: microcline and albite, 52%; sodalite, 21%; pyroxene, 14%; nepheline, 11%; accessory minerals, 2%.

Microcline, the most abundant constituent, tends to be tabular parallel to crystal axis *a* and to form rudely radiating groups, but does not show good crystal outline.   The cores of some of the microcline anhedra are somewhat clouded, but the margins are clear.   Much of it has been replaced by albite. In some grains the replacement is along irregular zones as shown in Fig. 1, but in others only the margins have been attacked.   Many of the small anhedra of albite show no multiple twinning, but most of the larger grains are well twinned.   Where the microcline has been almost entirely replaced, the

PLATE I
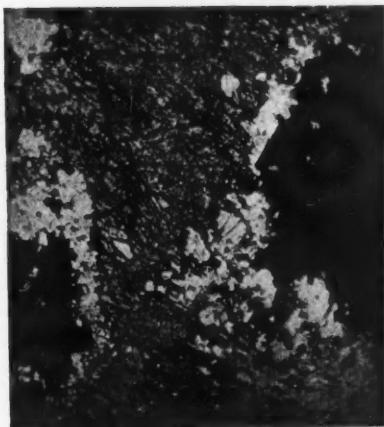
2A
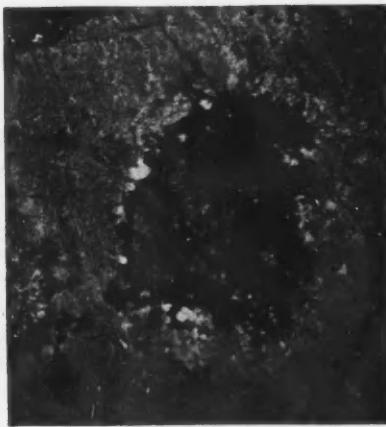
2B

1

3

FIG. 1.   *Radiating aggregate of microcline partly replaced by albite in the ditroite.* (A)×23.
Nicols×.
   FIGS. 2A AND 2B.   *Specimen B.   Fig. A shows the common relationship in which aegirine*
(middle of field) is separated from biotite (black) by a zone of light minerals.   B shows an excep-
tional arrangement in which an anhedron of aegirine is surrounded by biotite and both enclosed
within microcline microperthite.   ×23.
   FIG. 3.   *Ilmenite rods within magnetite.   From B.   Reflected and oblique light.*   ×23.
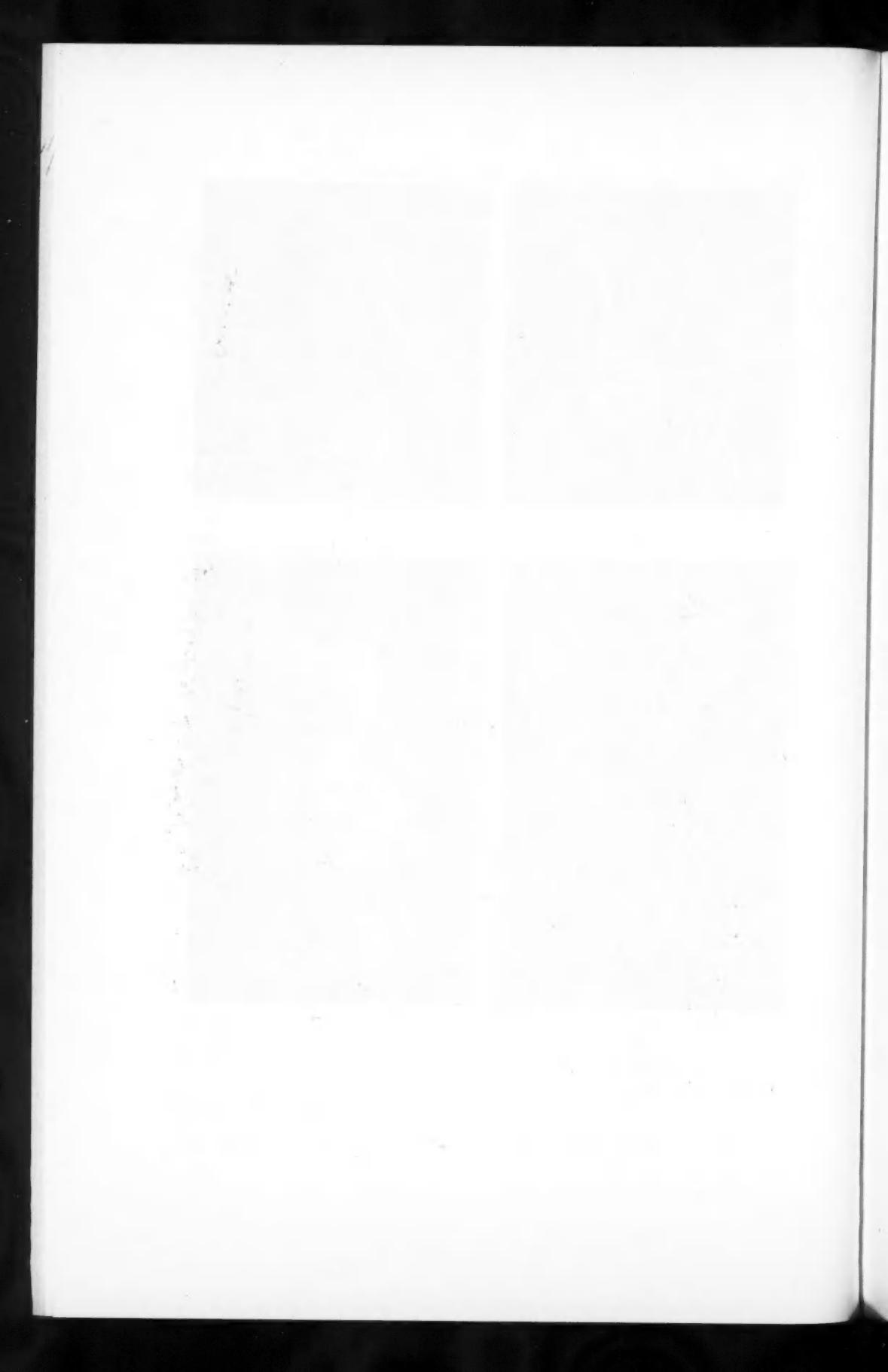
albite is lamellar and in somewhat diverging groups so that it resembles the cleavelandite found in granite-pegmatite dykes. Only a little albite appears to have formed away from microcline.

Aluminous aegirine, which does not show good crystal boundaries, is present in isolated rods, irregular bundles, or fibrous aggregates and appears to replace feldspar. It is unusual in that it is practically colorless, in this respect resembling rhombic pyroxene from which it differs, however, in possessing high indices and birefringence It shows very faint pleochroism in brown and green in the prismatic sections. The section normal to c shows nearly central emergence of α and a parting (not due to twinning) parallel to 100, bisecting the angles between the traces of the prismatic cleavage and at right angles to the trace of the optic-axial plane.

The lower index of refraction, α, determined by immersion is 1.72 and $\gamma - \alpha$, estimated in thin section from a grain showing central emergence of the optic normal, is about $.03$. The extinction angle, $\alpha \wedge c$, is $7°$. It is optically negative with an optic-axial angle of $65°$ and a marked dispersion $\rho > \nu$. The strong dispersion causes incomplete extinction in white light so the color changes from blue to brown on going through the position of extinction. In contact with perovskite it is an intense canary yellow with only appreciable differential absorption.

The chemical analysis of the rock given below as I shows an excess of Al_2O_3 over Na_2O, K_2O and CaO. Part of the Al_2O_3, as $NaAl(SiO_3)_2$, has undoubtedly replaced part of the Fe_2O_3 of the aegirine molecule. Jadeite occurs in omphacite. It is probably this molecule in the pyroxene that accounts for the value of α $.05$ below that of aegirine proper, a birefringence of about half of that of aegirine, and the absence of strong pleochroism.

Nepheline is found in water-clear or only slightly clouded grains interstitial to the feldspars. It is replaced around its margins by large individuals or granular aggregates of sodalite or a related mineral.

The sodalite contains small myrmekite-like anhedra of nepheline, microcline and albite which are parallel to adjacent grains of the corresponding minerals. Similar inclusions of microcline and albite are not found in nepheline, which suggests that the sodalite was formed at the expense of nepheline, microcline and albite along grain boundaries, particularly near nepheline. Some parts of the sodalite are a pale canary yellow but only where they are very close to the pyroxene and perovskite.

Zircon occurs in somewhat rounded and equidimensional grains. It is not appreciably radioactive judged by its effects on adjacent minerals. Perovskite is present in rounded isotropic grains of very high index. The cores of the larger grains are colorless, grading to light red at the margins. The smaller anhedra are entirely red and appear to be more radioactive than the larger colorless grains judging from the effect on adjacent minerals. Magnetite is in minute octahedra found near the pyroxene. Larger aggregates of magnetite, hematite, and magnetite oxidized to hematite, are interstitial to the silicate minerals. Careful search of polished surfaces failed to show any metallic sulphide. Uniaxial carbonate is found in two parageneses: in some places it is

older than, and surrounded by, pyroxene, in others it replaces feldspar. Where it is associated with the pyroxene it shows grains of a dark red, strongly absorptive mineral projecting into it from the margins. The mineral could not be identified definitely, but is probably an iron oxide. This suggests that the carbonate is iron-bearing, but it could not be isolated for definite determination. Three very small grains of an unidentified mineral were found in the 15 sections. The mineral has high indices of refraction and birefringence, a large optic-axial angle, a negative sign, and extinction angle of 45°. The rock is an aegirine-ditroite.

Specimen B. Nepheline-sodalite-cancrinite-syenite

Northeast corner of Northern Rhodesia, between the Loangwa River
   and the border of Nyassaland

The rock is coarse in grain. It is composed of microcline, albite, nepheline, sodalite, cancrinite, biotite, pyroxene, with smaller amounts of magnetite, ilmenite, hematite, pyrite, chalcopyrite, zircon and calcite.

The feldspars are pale mauve in color and show only simple twinning. Black biotite and pyroxene are the ferromagnesian minerals. Blue sodalite and nepheline with honey-yellow cancrinite are interstitial to the feldspars.

The microcline in thin sections is water-clear and shows the usual quadrille and Carlsbad twinning but is replaced along irregular branching veins by albite. This injection perthite is in marked contrast to the more regular structure of the microperthite formed by unmixing of a solid solution. In addition, small unorientated grains of albite occur in microcline near the grain margins, along fractures, and along the Carlsbad twinning junctions.

The nepheline is present in large grains completely or partly altered to cancrinite and sodalite. The alteration appears to start at the margins and proceed toward the centre of the grains, although, in some places, fractures in the nepheline have localized the formation of cancrinite. The sodalite, which also appears to have been replaced by the cancrinite, has some inclusions of natrolite.

Pyroxene, optically similar to that from the aegirine-ditroite, occurs in small amounts. In one thin section, it is surrounded by biotite apparently formed by reaction; in others, however, it is found without any reaction rim. See Figs. 2A and 2B.

Biotite, which is the abundant mafic mineral, is highly differentially absorptive and changes from a very dark green to an olive shade as the stage is rotated. The crystals are idiomorphic and appear to be of late development because in one place unbroken biotite is found in a minor shear zone, marked by the broken feldspars.

Magnetite, magnetite with intergrown ilmenite (Fig. 3), ilmenite, hematite, pyrite, and chalcopyrite are interstitial to the silicates. The pyrite appears to have replaced the oxides and has in turn been replaced by chalcopyrite (a few minute grains) and a hydrated iron oxide. Zircon is found in very small grains, but no perovskite was noted. Calcite replaces feldspar and, in some places, grains of calcite localized rims of cancrinite in nepheline.

Chemical Composition

The aegirine-ditroite (Specimen A) was analyzed for the writers by Miss Mary G. Keyes, formerly chemical assistant to Dr. Henry Washington at the Geophysical Laboratory, Washington, D.C. The results of this analysis are given as No. I in Table I—with it are given analyses of three other rocks for

TABLE I
COMPARISON OF ANALYSIS OF SPECIMEN A WITH ANALYSES OF OTHER ROCKS

Constituent	I	II	III	IV
	Per cent			
SiO_2	56.31	57.87	56.74	62.02
TiO_2	Tr	.48	.40	.31
Al_2O_3	19.89	18.46	19.32	18.71
Fe_2O_3	4.28	4.63	2.37	4.30
FeO	.29	.40	1.65	.10
MnO	.16		.07	.15
MgO	.26	.61	.27	.40
CaO	.74	1.03	1.98	.86
Na_2O	8.33	8.83	8.05	6.90
K_2O	5.75	5.74	5.88	4.93
H_2O+	.68	.90	1.12	.80
H_2O-	.13	.70	.32	.31
CO_2	1.27		1.50	none
P_2O_5	n. d.	.14	.03	.24
ZrO_2	.16		.02	.06
SO_3	.19		.12	.02
Cl	1.13	.62		none
BaO	Tr		.16	.02
	99.57	100.41	100.17	100.13

I. *Ditroite. Specimen A. Analyst, Mary G. Keyes.*
II. *Phonolite, Patagwa River, near Utanjilva, Nyassa. Analyst, E. Lehmann, (2, p. 107).*
III. *Cancrinite syenite, Beaver Creek, Uncompahgre quadrangle, Col. with SrO .12 and S .05. Analyst, G. Steiger (3, p. 295).*
IV. *Trachyte, Puu Anahulu, Hawaii. Analyst, H. S. Washington (4, p. 108).*

TABLE II
THE NORM OF NO. I

Constituent	%	Constituent	%
Orthoclase (Or)	34.47	Sodium Carbonate (Ne)	1.38
Albite (Ab)	47.68	Zircon (Z)	.18
Anorthite (An)	none	Olivine (Ol)	.56
Nepheline (Ne)	2.27	Magnetite (Mt)	.93
Corundum (C)	3.47	Hematite (Hm)	3.68
Halite (Hl)	1.76	Calcite (Cc)	1.30
Thenardite (Th)	.28		
			97.96

comparison. It is interesting to note that analysis II, of a phonolite from near Utanjilva, Nyassaland, is almost identical with that of aegirine-ditroite (Specimen A) from Northwest Rhodesia. The two localities must be 500

miles or more apart but as both are rather unusual in chemical composition, it would suggest that they belong to the same petrographical province or to two petrographical provinces which resemble one another closely.

The norm of No. I is shown in Table II. The low summation of this norm is due to the omission of oxygen taken from Na_2O to form $NaCl$ and to the water which must be added.

It will be noticed that this rock is distinctly "non modal", that is to say, the norm differs very considerably from the mode or actual mineral composition as seen under the microscope. This same divergence has been noted by Washington in the case of the Trachyte from Puu Anahulu in Hawaii, his analysis of which is given as IV in Table I, and which resembles the rock now under consideration although considerably higher in silica. Both analyses have been very carefully made and checked and there is every reason to believe that they are correct and, as Dr. Washington states, this non modal character in both of these rocks, which are similar in character, is "difficult to understand". It may possibly be connected in some measure with the peculiar composition of the pyroxene present whose chemical composition is as yet unknown but which will be further studied.

Comparison with the Syenite of Ditro

The abundance of potassic feldspar shows that the rocks are related to the Foya rather than the Litchfield or Canada type of nepheline syenite.

An examination of the nepheline syenites in the petrological collection at McGill University shows no one that is identical with either specimen from Africa. The aegirine-ditroite resembles to some extent the finer-grained variety of ditroite from Ditro, except that the feldspar of the Ditro rock is somewhat more glassy in appearance, and the ferromagnesian minerals are black, whereas those of the African specimen are pale green. Under the microscope the texture is different: the sodalite of the ditroite is in equidimensional anhedra; the aegirine is a very strongly absorptive variety, and has a reaction rim of the blue-green amphibole known as hastingsite; and titanite is abundant.

The feldspar of the coarser African rock resembles in color that of the Laurdalite from Laurvig but is, of course, microcline.

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